CHAPTER I

INTRODUCTION

1.1 Introduction

There is a growing interest in developing engineered actuation systems that have properties more in common with soft biological materials such as muscles and tendons than with traditional engineering materials. Interest in hydrogels has gained momentum recently because these materials can undergo a reversible phase transformation that results in dramatic volumetric swelling and shrinking upon exposure and removal of a stimuli.[1]

Polymer gels have attracted attention as "intelligent or smart materials" because of their peculiar material forms. They consist of an elastic crosslinked network and a fluid filling the interstitial spaces of the network. Polymer hydrogels can change their volume and shape reversibly depending on several external physicochemical factors; such as, temperature, solvent composition, pH, and ionic concentration. Therefore, the large volume or shape change of a polymer gel, induced by supplying thermal, chemical, or electrical energy, offers various possibilities for advanced functional polymers. Among these possibilities, electric-sensitive polymer hydrogels actuated by an electric stimulus seem to be particularly interesting because mechanical energy can be triggered by electrical signals. The hydrogels that respond to electrical stimulation with a change in shape or size are called electroactive polymers (EAPs). No other kind of materials attains comparable volumetric expansion. Their practical advantages as actuators or artificial muscles are flexibility, light weight, tolerance against fracture, and easy molding compared with conventional electromechanical ceramics. To improve the physical and chemical properties of gels, two or more polymer backbone components are often mixed to form a multicomponent material.

The influence of an electric potential on the bending behavior of polyelectrolyte gels has been studied with various hydrogel systems. Kim et al. reported that a poly(vinyl alcohol)/chitosan (PVA/chitosan) IPN hydrogel exhibited the electro-sensitive behavior in an aqueous NaCl solution.[2] The bending angle and the bending speed of the PVA/chitosan hydrogel increased with an increasing applied voltage and the concentration of the aqueous NaCl solution. They also reported the electrical response characterization of chitosan/polyacrylonitrile hydrogels in NaCl solutions.[3] They found that the hydrogels exhibited bending behavior upon the application of an electric field and showed the variation of bending angle as a function of the applied electrical stimulus. Sun and Mak demonstrated that a hydrogel fiber based on chitosan/poly(ethylene glycol) displayed mechanoelectro-chemical (MEC) behavior.[4] Properties of electro-responsive poly(vinyl alcohol)/ poly(acrylic acid) IPN hydrogels, under an electric stimulus, were also studied by Kim et al.[5]. They reported that an equilibrium bending angle and a bending speed of PVA/PAA IPN hydrogels increased with an applied voltage and the content of the PAA network, providing negatively charged ionic groups within the IPN hydrogel. S. J. Kim. and coworkers[6] studied shape change characteristics of poly(acrylic acid)/poly(vinyl sulfonic acid) in electric field. They have shown the stimuli-sensitive behavior of hydrogels as a function of temperatures and pH, in an applied electric field. The swelling ratio increased with increasing temperature and pH. The hydrogels exhibited volume changes that were sensitive to external stimuli, such as temperature, pH, and electric field.

The model of synthetic muscle using shrinking behavior of an electric field-controlled gel was published in 1972.[7] The system used a weakly acidic contractile gel sensitive to pH change. The response of the gel as a function of pH, solution concentration, compartment size, certain cations, and gel fabrication were studied. It is necessary to improve the tensile force and response time of the system. Of most interest in the bending deformation of a gel in an electric field is the production of a large deflection with a relatively high speed. Therefore, the bending deformation has been applied to the fabrication of systems that exhibit biological motion. Figure 1.1

shows a mechanical hand with four gel fingers. The fingers bend inward using differential swelling at the anode. The hand can hold a 9 g quail egg and remove it from the surrounding solution.[8] An artificial fish with a tail of gel film, which can swim at a velocity of 2 $cm.s^{-1}$ under an AC electric field of 0±5 Hz, has been designed. The bending of the gel tail is converted into a one-dimensional motion[9] (Figure 1.2).

Figure 1.1 Robot hand with four smart gel fingers holding a quail egg[9]

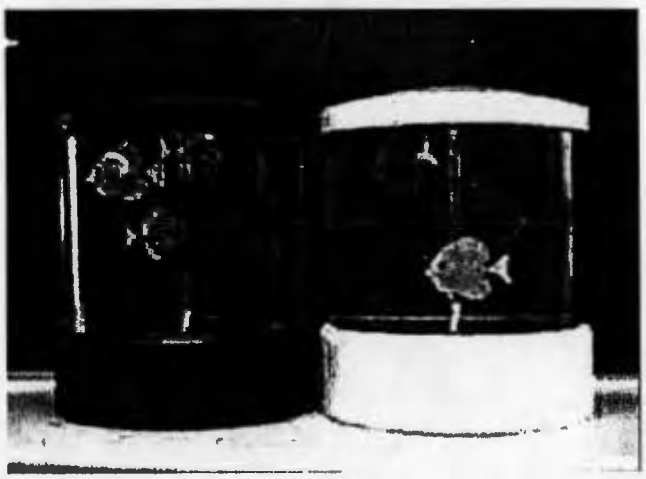

Figure 1.2 An artificial fish with a tail of gel film[10]

A polymer gel with two hooks (Figure 1.3), which performs a looping action, has also been fabricated.[11] The two hooks are hung on a plastic ratchet bar. The motion is based on bending due to the interaction between the surfactant molecules in

a solution and the gel network. The gel moves at a velocity of 25 $cm.min^{-1}$ in solution. The three biomimetic systems using electric field associated gel deformation described above function only in solution. The next target is a system that will operate in air. An advance in gel devices has been the design of electrically driven fingers that work in air[12]: a mechanical hand has been constructed with two smart gel fingers which can bend inward simultaneously on the application of a DC electric field, and can catch a piece of paper weighing 0.2 g.

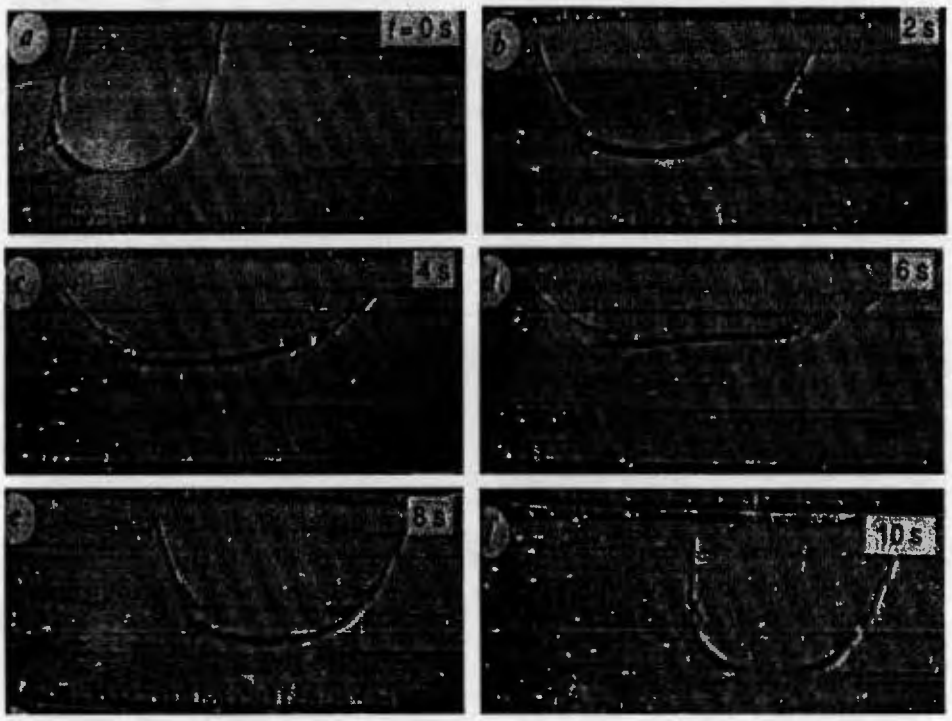

Figure 1.3 A polymer gel with two hooks[11]

Otake, M. and coworkers proposes a method to generate novel motions of mollusk-type deformable robots made of electro-active polymer gel. Simulation and experimental results show that large transformations can be obtained with multiple electrodes in a planar configuration. They have designed a starfish-shaped gel robot that can turn over using spatially varying electric fields[13] (Figure 1.4).

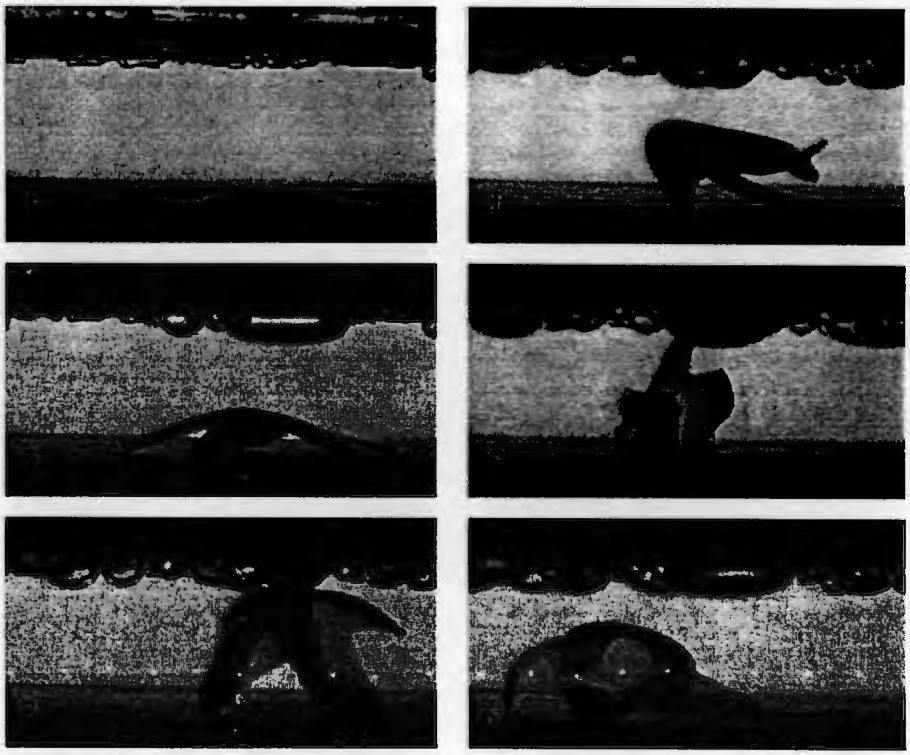

Figure 1.4 A starfish gel robot that turns over[13]

Their experimental results showed the reversibility of the bending behavior under an applied electric field. They also reported that a bending curvature was proportional to the intensity of an applied electric potential. The response of these gels is usually slow and it is expected that the response time will be limited by the diffusion time of ions through the gel. A much faster response would be expected from fibers or thin films, and practical artificial muscles will probably require a finely divided structure of interleaved electrodes and gels.

Therefore, to realize a powerful actuator or a material close to skeletal muscles, it was necessary to have both fast and sensitive electric responses and a high degree of mechanical strength for a polymer gel. The IPN system could be a promising candidate to meet these requirements because it could induce quite strong mechanical properties.[5]

To synthesize a powerful actuator or a material close in nature to skeletal muscles, it was necessary for the polymer gel to have both fast and sensitive electrical responses and strong mechanical strength. From the viewpoint of mechanical engineering, great hopes are set on these materials as new actuators, especially in the fields of robotics. In point of fact, the realization of lightweight, soft touch, and powerful actuators is an important factor. For this thesis, chitosan is chosen because it can contain much water. Part of this water is tightly bound to the polymer and the rest is present as free water. Water in crosslinked and uncrosslinked chitosan gives rise to a three-dimensional network. Chitosan based hydrogels exhibit good biocompatibility, low degradation and processing ease.[14] Another polymer, poly(acrylic acid) is a synthetic polyelectrolyte that shows pH and electric-responsive.[15] Barakol is extracted from the leaves and flowers of *Cassia siamea*. It can improve rapid response of hydrogel film with environmental stimuli.

This thesis proposes a novel electric-sensitive polymer hydrogel prepared from chitosan, poly(acrylic acid), barakol and crosslinking agents. Both chitosan and barakol are natural material available in Thailand and are not expensive. Their use in smart materials is a novel application for both of them.

1.2 Objective

The objective of this thesis is to make a smart material in the form of hydrogel films with fast and sensitive electrical responses and strong mechanical strength. The material is prepared from chitosan, poly(acrylic acid), barakol and crosslinking agents. Various parameters including the ratio of component materials, concentration of surrounding solution and electrical voltage are taking into account.