

DOKUZ EYLÜL UNIVERSITY
GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES

**COMPARISON OF ELECTROMECHANICAL
BEHAVIOURS OF NANOPARTICLES LOADED
POLYMERIC FILMS**

by
İbrahim ŞEN

December, 2014
İZMİR

**COMPARISON OF ELECTROMECHANICAL
BEHAVIOURS OF NANOPARTICLES LOADED
POLYMERIC FILMS**

**A Thesis Submitted to the
Graduate School of Natural and Applied Sciences of Dokuz Eylül University
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Chemistry Program**

**by
İbrahim ŞEN**

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İZMİR**

M.Sc THESIS EXAMINATION RESULT FORM

We have read the thesis entitled “**COMPARISON OF ELECTROMECHANICAL BEHAVIOURS OF NANOPARTICLES LOADED POLYMERIC FILMS**” completed by **İBRAHİM ŞEN** under supervision of **ASSOC.PROF.DR.YOLDAŞ SEKİ** and we certify that in our opinion it is fully adequate, in scope and in quality, as a thesis for the degree of Master of Science.



Assoc. Prof. Dr. Yoldaş Seki

Supervisor



Prof. Dr. Mehmet Kadir Yurdakog

(Jury Member)



Assoc. Prof. Dr. Kutlay Sever

(Jury Member)



Prof.Dr. Ayşe OKUR

Director

Graduate School of Natural and Applied Sciences

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COMPARISON OF ELECTROMECHANICAL BEHAVIOURS OF NANOPARTICLES LOADED POLYMERIC FILMS

ABSTRACT

This work presents a facile preparation of a flexible gel material from a solution of cellulose in an ionic liquid of 1-butyl-3-methylimidazolium chloride and dimethylacetamide using solution casting method. Then graphene at different ratios (0.1, 0.25, 0.375 and 0.5 percent) was dispersed in obtained solution by the help of ultrasonic homogenizator. The thermal stability of the films was investigated by thermogravimetric analysis. The effect of graphene treatment of Cellulose-based films on electrical conductivity was examined. The variations in chemical functional groups and crystallographic properties were evaluated by Fourier transform infrared (FTIR), X-ray diffraction (XRD). The morphological observations of Cellulose based films and graphene treated Cellulose based films were conducted by scanning electron microscopy (SEM). After determination of film properties, for actuators studies of films, both sides the films were gold-coated. The effect of gold coating on tensile strength and Young modulus films were examined as well. Besides, electroactive behaviour of the coated films under DC was investigated. DC excitations of 3, 5, and 7 Volts were used. The tip displacement was measured and time constant was calculated. It was obtained that there is a nonlinear relationship between graphene content and electroactive characteristics of IPMC actuators such as the maximum tip displacement and time constant. For DC excitations of 3V, the actuator made from cellulose based film containing 0.5 percent graphene in all actuators exhibited the greatest maximum tip displacement values. The maximum tip displacements for the cellulose based film containing 0.5 percent graphene demonstrated the following values: 1.4 mm for 3V, -1.4 mm for (negative)3V, 1.2 mm for 5V, -0.65 mm for (negative)5V, 0.5 mm for 7V and -0.7 mm for (negative)7V, respectively.

Keywords: Cellulose, ionic liquids, Graphene, electroactive behaviour

NANOPARÇACIK TAKVİYELİ POLİMERİK FİLMLERİN ELEKTROMEKANİK DAVRANIŞLARININ KARŞILAŞTIRILMASI

ÖZ

Bu çalışmada, selülozun çözücü olarak kullanılan 1-butil-3- metil imidazonyum klorür ve dimetilasetamid içinde çözünmesi ile hazırlanmış çözeltinin petri kabına dökülmesiyle esnek bir jel materyali hazırlanmıştır. Farklı oranlardaki grafen (yüzde 0,1, 0,25, 0,375 ve 0,5) yukarıda bahsedilen selüloz çözeltisinin içerisinde ultrasonik homojenetörün yardımıyla dağıtıldı. Sentezlenen selüloz ve grafen katkılı selüloz filmlerin termal kararlılığı ,Termogravimetrik analiz yöntemiyle incelenmiştir. Grafen katkısının selülozik filmlerin elektriksel iletkenliklerine olan etkisi incelenmiştir. Fonksiyonel gruplar ve kristalografik özelliklerdeki değişim Kızıl Ötesi spektrometresi ve X-Işını kırınımı ile belirlenmiştir. Üretilen filmlerin morfolojik özellikleri taramalı elektron mikroskobu ile yapılmıştır. Filmlerin karakterizasyonun ardından filmlerin elektroaktif özelliklerinin belirlenmesi için , filmlerin her iki yüzeyleri altın film ile kaplanarak iyonik polimer metal kompozitler (IPMC) üretilmiştir. Altın kaplamanın filmlerin çekme dayanımı ve Young modülünü nasıl değiştirdiği çekme analizi ile tespit edilmiştir.. Altın kaplanmış filmlerin DC voltaj altındaki elektroaktif davranışları incelenmiştir.. DC voltaj çıkışları 3, 5 ve 7 volt olarak kullanılmıştır. Grafen katkılı IPMC aktüvatörlerin maksimum uç yer değiştirmeleri ve zaman sabitleri belirlenmiştir.Bu özellikler ile grafen miktarı arasındadoğrusal olmayan bir ilişki gözlenmiştir. DC voltaj çıkışı 3V için yüzde 0,5 grafen içeren selülozik tabanlı yapılmış aktüvatörün en büyük uç yer değiştirme gösterdiği belirlenmiştir. Yüzde 0,5 grafen içeren selüloz tabanlı filmin maksimum uç yer değiştirmeleri DC voltaj çıkışları 3V için 1,4mm, (negatif)3V için-1,4mm, 5V için 1,2mm, (negatif)5V için -0,65mm, 7V için 0,5mm ve (negatif)7V için -0,7mm olarak bulunmuştur.

Anahtar kelimeler: Selüloz, iyonik sıvı, Grafen, elektroaktif davranış

CONTENTS

	Page
M.Sc THESIS EXAMINATION RESULT FORM.....	ii
ACKNOWLEDGMENTS	iii
ABSTRACT	iv
ÖZ	v
LIST OF FIGURES	viii
LIST OF TABLES	xii
CHAPTER ONE-INTRODUCTION	1
1.1 Electroactive Polymers.....	1
1.1.1 Ionic Polymer Metal Composites	2
1.2 Ionic Liquids.....	6
1.2.1 History	7
1.2.2 Structure of Ionic Liquids.....	9
1.2.2.1 Cations	9
1.2.2.2 Anions	10
1.2.3 Use and Applications of IonicLiquids	11
1.3 Graphene	12
1.3.1 Carbon Allotropes.....	12
1.3.2 Properties of Graphene	15
1.4 Cellulose.....	16
1.4.1 The Dissolution Mechanism of Cellulose in 1-n-Butyl-3-Methylimidazolium chloride.....	17
CHAPTER TWO-EXPERIMENTAL METHOD AND INSTRUMENTATION	19
2.1 Material	19

2.2 Fabrications of Cel-Cl-DMAC and Cel-Cl-DMAC-Gr.....	20
2.3 FTIR Analysis	21
2.4 Thermogravimetric Analysis (TGA)	21
2.5 X-Ray Diffraction (XRD) Analysis.....	21
2.6 Scanning Electron Microscope (SEM) Observations.....	22
2.7 Mechanical Properties	22
2.8 Electrical Properties	23
2.9 Electroactive Properties.....	23
2.9.1 Experimental Setup.....	23
2.9.2 Fabrication of IPMC Actuators	24
2.9.3 Experiments	26
CHAPTER THREE-RESULTS AND DISCUSSIONS	27
3.1 FTIR Analysis	27
3.2 Thermogravimetric Analysis (TGA).....	30
3.3 X-Ray Diffraction (XRD)Analysis.....	35
3.4 Scanning Electron Microscope (SEM).....	41
3.5 Mechanical Properties	47
3.6 Electrical Properties	50
3.7 Electroactive Properties.....	51
CHAPTER FOUR-CONCLUSIONS	70
REFERENCES.....	72

LIST OF FIGURES

	Page
Figure 1.1 The classification of active polymers.....	2
Figure 1.2 Production of EAP	3
Figure 1.3 The actuation behaviour of EAP (a) smart structures,(b) underwater robots , (c) fish-robots (d) micro-pumps.	4
Figure 1.4 Structure of nafion(a), aciplex(b) and flemion(c)	5
Figure 1.5 Migration of hydrated cations induced by electric potential bends the IPMC toward the anode.....	6
Figure 1.6 IL publications (on Dec30, 2013) determined from the ISI Web of Science in the last twenty years.....	8
Figure 1.7 Mostly commonly anion and cation	11
Figure 1.8 Applications of Ionic liquids	12
Figure 1.9 Diamond structure	13
Figure 1.10 Graphite structures.....	13
Figure 1.11 Mother of all graphitic forms. Graphene is a 2-D building material for carbon materials with other dimensions including zero dimensions (fullerenes), one dimension (carbon nanotubes) and three dimensions (graphite)	15
Figure 1.12 The structure of cellulose.....	16
Figure 1.13 Dissolution of cellulose in ionic liquids ([C4mim] δ^+ Cl δ^- :BMIMCl)..	18
Figure 2.1 Schematic representation of the structures of BmimCl(a) and DMAC(b)	19
Figure 2.2(a) Ultrasonic processor (b) Film casting knife	20
Figure 2.3 Different Gr loaded films.....	21
Figure 2.4The experimental setup for measuring actuation of IPMC actuator.....	233
Figure 2.5 The vision system for measuring actuation of IPMC actuator.	24
Figure 2.6 Production of IPMC actuators	25
Figure 2.7 Actuators samples.....	26

Figure 3.1 FTIR spectra of samples: a) cellulose, b) Cel-Cl-DMAC, c) Cel-Cl-DMAC-%0.1Gr, d) Cel-Cl-DMAC-0.25Gr, e) Cel-Cl-DMAC-0.375Gr, f) Cel-Cl-DMAC-0.5Gr	29
Figure 3.2 TGA profile for the BmimCl	31
Figure 3.3 TGA profile for the cellulose.....	31
Figure 3.4 TGA profile for the Cel-Cl-DMAC	32
Figure 3.5 TGA profile for the Cel-Cl-DMAC-0.1Gr	32
Figure 3.6 TGA profile for the Cel-Cl-DMAC-0.25Gr	34
Figure 3.7 TGA profile for the Cel-Cl-DMAC-0.375Gr	34
Figure 3.8 TGA profile for the Cel-Cl-DMAC-0.5Gr	35
Figure 3.9 X-ray diffraction pattern of graphene	36
Figure 3.10 X-ray diffraction pattern of cellulose	36
Figure 3.11 Degree of CI of cellulose, Cel-Cl-DMAC and Gr loaded Cel-Cl-DMAC using Segal's equation.....	37
Figure 3.12 X-ray diffraction pattern of Cel-Cl-DMAC.....	39
Figure 3.13 X-ray diffraction pattern of Cel-Cl-DMAC -0,1Gr	39
Figure 3.14 X-ray diffraction pattern of Cel-Cl-DMAC -0,25Gr	40
Figure 3.15 X-ray diffraction pattern of Cel-Cl-DMAC -0,375Gr	40
Figure 3.16 X-ray diffraction pattern of Cel-Cl-DMAC -0,5Gr	41
Figure 3.17 SEM images of Cel-Cl-DMAC at magnifications of 1000x and 5000x.	42
Figure 3.18 SEM images of Cel-Cl-DMAC at magnifications of 10000x and 20000x	43
Figure 3.19 SEM images of Cel-Cl-DMAC at magnification of 50000x	44
Figure 3.20 SEM images of Cel-Cl-DMAC-0.1Gr at magnification of 20000x	45
Figure 3.21 SEM images of Cel-Cl-DMAC-0.25Gr at magnification of 10000x	45
Figure 3.22 SEM images of Cel-Cl-DMAC-0.375Gr at magnification of 10000x ..	46
Figure 3.23 SEM images of Cel-Cl-DMAC-0.5Gr at magnification of 10000x	46
Figure 3.24 Effect of Gr loading on tensile strength of gold coated Cel-Cl-DMAC.	49
Figure 3.25 Effect of Gr loading on Young's modulus of gold coated Cel-Cl-DMAC	50
Figure 3.26 Electrical conductivity of Cel-Cl-DMAC and loaded Cel-Cl-DMAC films	51

Figure 3.27 The time evolution of the tip displacement (time response) of Cel-Cl-DMAC(3v).....	54
Figure 3.28 The time evolution of the tip displacement (time response) of Cel-Cl-DMAC(-3v)	54
Figure 3.29 The time evolution of the tip displacement (time response) of Cel-Cl-DMAC-0.1Gr(3v)	55
Figure 3.30 The time evolution of the tip displacement (time response) of Cel-Cl-DMAC-0.1Gr(-3v).....	55
Figure 3.31 The time evolution of the tip displacement (time response) of Cel-Cl-DMAC-0.25Gr(3v)	56
Figure 3.32 The time evolution of the tip displacement (time response) of Cel-Cl-DMAC-0.25Gr(-3v).....	56
Figure 3.33 The time evolution of the tip displacement (time response) of Cel-Cl-DMAC-0.25Gr(5v)	57
Figure 3.34 The time evolution of the tip displacement (time response) of Cel-Cl-DMAC-0.25Gr(-5v).....	57
Figure 3.35 The time evolution of the tip displacement (time response) of Cel-Cl-DMAC-0.5Gr(3v)	58
Figure 3.36 The time evolution of the tip displacement (time response) of Cel-Cl-DMAC-0.5Gr(-3v).....	58
Figure 3.37 The time evolution of the tip displacement (time response) of Cel-Cl-DMAC-0.5Gr(5v)	59
Figure 3.38 The time evolution of the tip displacement (time response) of Cel-Cl-DMAC-0.5Gr(-5v).....	59
Figure 3.39 The time evolution of the tip displacement (time response) of Cel-Cl-DMAC-0.5Gr(7v)	60
Figure 3.40 The time evolution of the tip displacement (time response) of Cel-Cl-DMAC-0.5Gr(-7v).....	60
Figure 3.41 The time evolution of the tip displacement (time response) of Cel-Cl-DMAC(5v).....	61
Figure 3.42 The time evolution of the tip displacement (time response) of Cel-Cl-DMAC(-5v)	62

Figure 3.43 The time evolution of the tip displacement (time response) of Cel-Cl-DMAC(7v).....	62
Figure 3.44 The time evolution of the tip displacement (time response) of Cel-Cl-DMAC(-7v)	63
Figure 3.45 The time evolution of the tip displacement (time response) of Cel-Cl-DMAC-0.1Gr(5v)	63
Figure 3.46 The time evolution of the tip displacement (time response) of Cel-Cl-DMAC-0.1Gr(-5v).....	64
Figure 3.47 The time evolution of the tip displacement (time response) of Cel-Cl-DMAC-0.1Gr(7v)	64
Figure 3.48 The time evolution of the tip displacement (time response) of Cel-Cl-DMAC-0.1Gr(-7v).....	65
Figure 3.49 The time evolution of the tip displacement (time response) of Cel-Cl-DMAC-0.25Gr(7v)	65
Figure 3.50 The time evolution of the tip displacement (time response) of Cel-Cl-DMAC-0.25Gr(-7v).....	66
Figure 3.51 The time evolution of the tip displacement (time response) of Cel-Cl-DMAC-0.375Gr(3v)	66
Figure 3.52 The time evolution of the tip displacement (time response) of Cel-Cl-DMAC-0.375Gr(-3v).....	67
Figure 3.53 The time evolution of the tip displacement (time response) of Cel-Cl-DMAC-0.375Gr(5v)	67
Figure 3.54 The time evolution of the tip displacement (time response) of Cel-Cl-DMAC-0.375Gr(-5v).....	68
Figure 3.55 The time evolution of the tip displacement (time response) of Cel-Cl-DMAC-0.375Gr(7v)	68
Figure 3.56 The time evolution of the tip displacement (time response) of Cel-Cl-DMAC-0.375Gr(-7v).....	69

LIST OF TABLES

	Page
Table 1.1 Comparison of ionic liquids with organic solvents.....	7
Table 1.2 The properties of ILs.....	9
Table 1.3 Some properties of carbon allotropes.....	14
Table 1.4 Properties of graphene ,carbon nanotube and diamond	16
Table 3.1 The main absorption bands for the samples.....	27
Table 3.2 TGA data for the samples	33
Table 3.3 The Crystallite size for the samples	38
Table 3.4 Mechanical properties of Cel-Cl-DMAC and Gr loaded Cel-Cl-DMAC..	49
Table 3.5 The maximum tip placements (mm) of Cel-Cl-DMAC and Gr loaded Cel- Cl-DMAC actuators when excited with 3, 5 and 7 volts	61
Table 3.6 Time constants (second) of Cel-Cl-DMAC and Gr loaded Cel-Cl-DMAC actuators when excited with 3, 5 and 7 volts.....	61

CHAPTER ONE

INTRODUCTION

1.1 Electroactive Polymers

Nowadays, technological advancements and conventional materials were (such as alloys and metal) replaced by polymers in such areas as aerospace, automobiles, electronics and household goods. Moreover polymer materials are more attractive properties than inorganic materials. Those properties are inexpensive, pliable, lightweight, fracture tolerant and rapidly processed and fabricated. For several decades, research is presented that they respond to external stimuli by size or changing shape. Such stimuli

- pH
- Light
- Electrical field
- A magnetic field
- Temperature etc.

These smart polymers can aggregately be called active polymers.

According on the type of running, the materials used are usually categorized as electro active polymers (EAPs) and non-electrically deformable polymers. An important non-electrically deformable polymers are chemically activated polymers, shape-memory polymers, inflatable structures, magnetically activated polymers, light-activated polymers, and thermally activated gels.

Polymers which change shape in respond to electrical stimulus are called electro active polymers(EAP) and are categorized depending on the mechanism liable for actuation as electronic EAPs that are wagged by coulomb forces or electric field or ionic EAPs that change shape by diffusion or mobility of their conjugated substances and ions A important active polymers are shown in Figure 1.1 (Kim & Tadokoro, 2007).

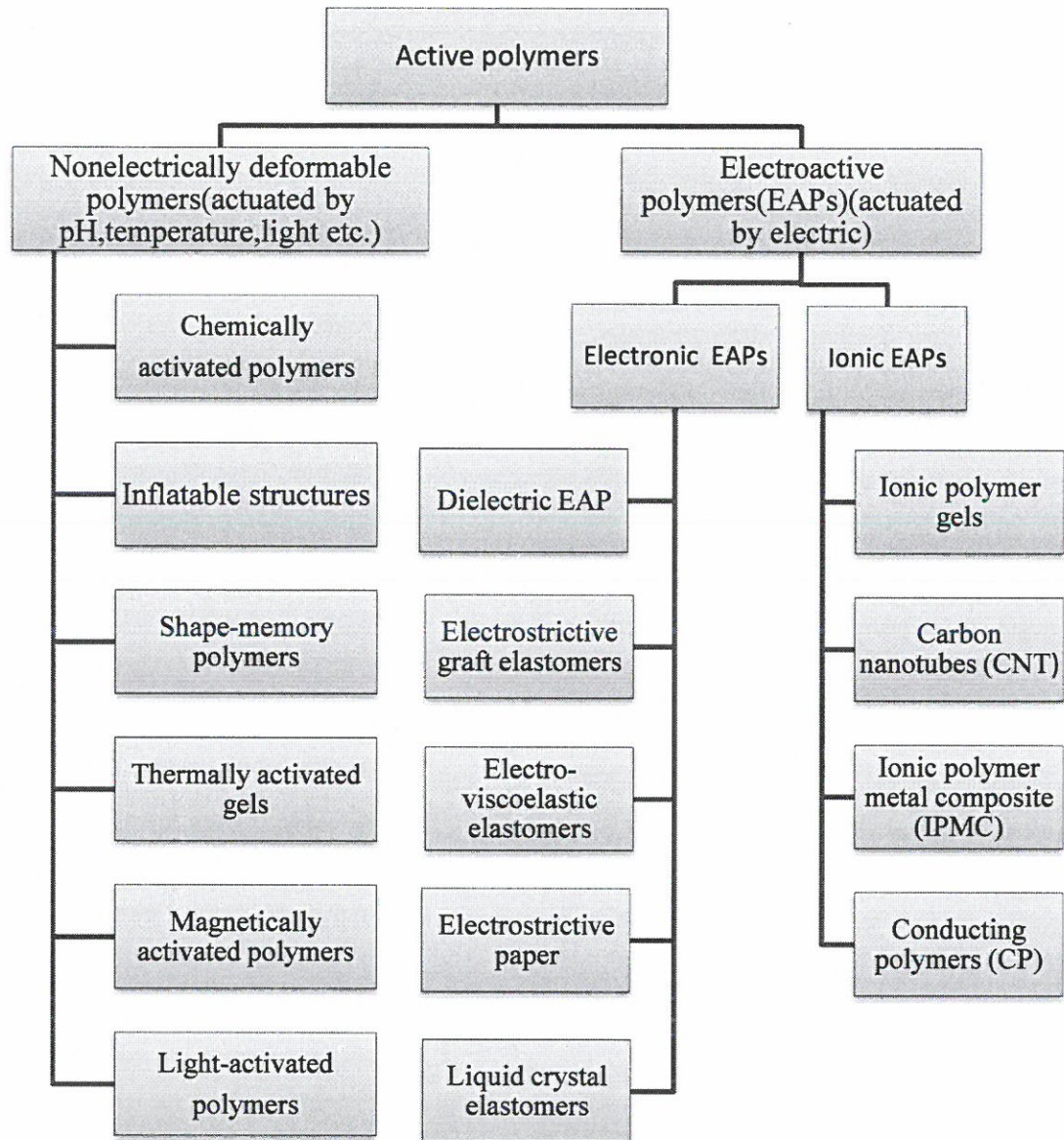


Figure 1.1 The classification of active polymers

1.1.1 Ionic Polymer Metal Composites

Ionic polymer–metal composites, in which they are categorized as smart materials which can generate a useful response and sense changes in the environment, can change their shapes by the movements of ions due to an external electric field (Kim, 2007; Lee & Yoo, 2011). Mostly, an IPMC takes place in a electro active

polymer(EAP) with metal electrodes on both sides (He et al, 2012) The structure of IPMC are shown in Figure 1.2

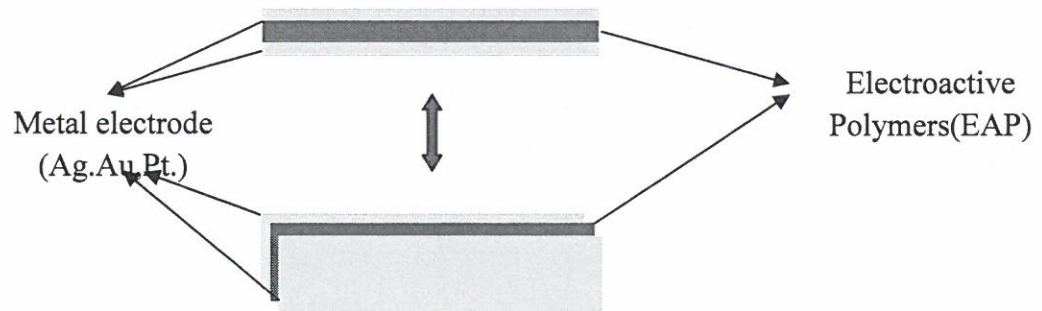


Figure 1.2 Production of EAP

. They have advantages, which are,

- Large bending deformation,
- High reliability ,
- Low-voltage operation,
- Flexibility
- Sensing capability (Jeon, Yeom & Oh, 2008; Lee & Yoo, 2011)
- Lightness,
- Softness(Akle, Bennett & Leo, 2006)

Some applications are (see Figure 1.3)

- smart structures (see Figure 1.3 (a)) (Shahinpoor, Bar-Cohen, Simpson & Smith, 1998)
- bio-medical devices
- bio-mimetic robots(Jeon, Yeom & Oh, 2008)
- artificial muscles
- fish-robots (see Figure 1.3 (c)),
- underwater robots (see Figure 1.3 (b)) (Chen, Um & Bart-Smith, 2011),
- micro-pumps (see Figure 1.3 (d)) (Shahinpoor & Kim, 2005; Du, Tang, Zhou & Xie, 2011)

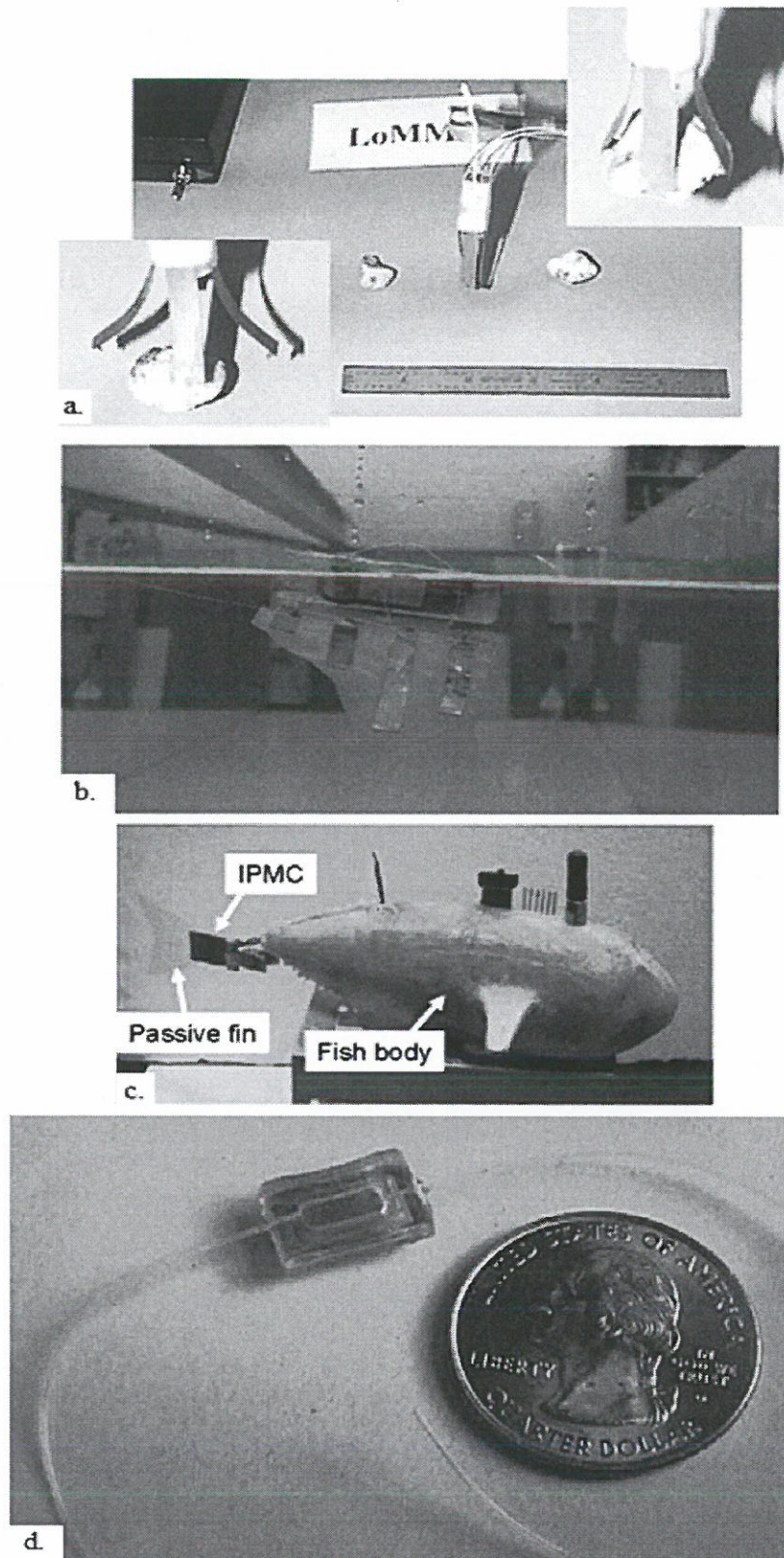
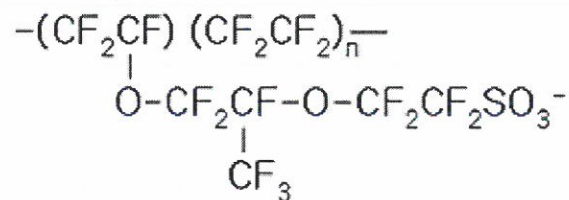


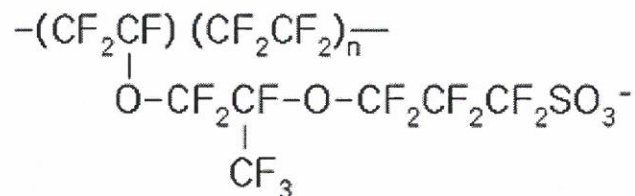
Figure 1.3 The actuation behaviour of EAP (a) smart structures,(b) underwater robots , (c) fish-robots (d) micro-pumps.

Generally, the EAP is made by forming electrodes on a Aciplex™, Nafion™ and Flemion™ (see Figure 1.4 a, b and c) (Lee, Jeon & Cha, 2010) membranes which are composed of a perfluorinated ionomer membrane and carboxylic acid ion exchange membranes and saturating the membrane with water (Akle, Bennett & Leo, 2006; Jo, Pugal, Oh, Kim & Asaka, 2013). When the electric field is impounded through the IPMC's thickness, the cations inside the ion exchange membrane put across solvent molecules towards the cathode and create bending of the actuator. It can undergo large bending deformation in reply to an electric potential applied across its thickness in aqueous environment (Fang, Ju & Lin, 2007).

(a)



(b)



(c)

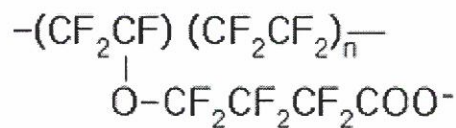


Figure 1.4 Structure of nafion(a), aciplex(b) and flemion(c)

The basically actuating principle of IPMC, when an electric field is applied on the metal electrodes, which brings about the hydrated cations inside the IPMC to migrate to the cathode (see Figure 1.5). Consequently, the IPMC bends toward the anode in so far as the asymmetrical swelling of the EAP induced by the cations. On the contrary the asymmetric distribution of electric charges in the EAP which is caused

by deforming the IPMC converts an electrical signal that gradually decreases with time(Enikov & Seo, 2005; Fang, Lin & Ju, 2010)

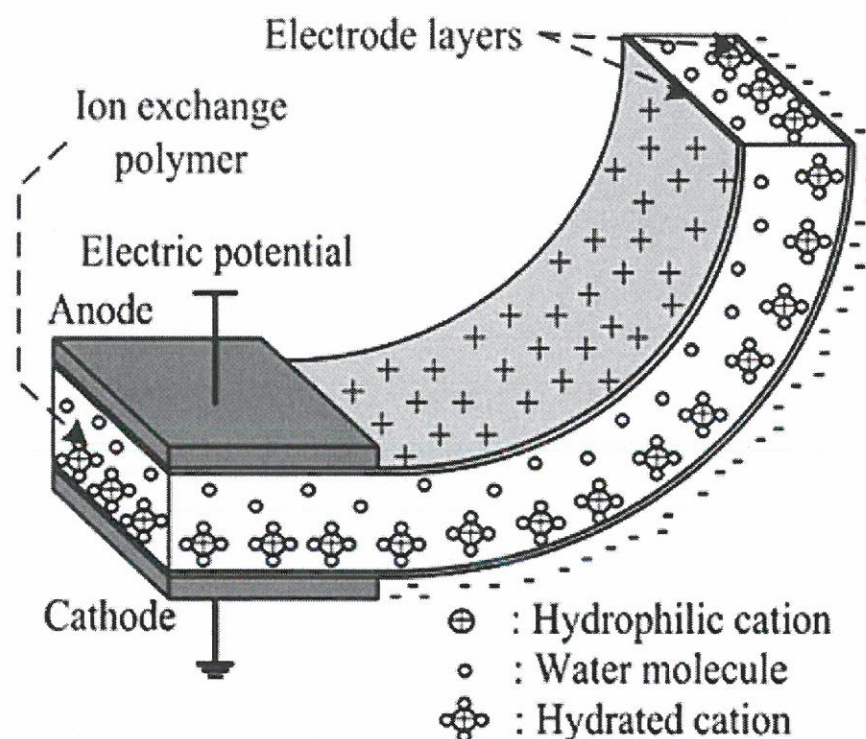


Figure 1.5 Migration of hydrated cations induced by electric potential bends the IPMC toward the anode

1.2 Ionic Liquids

Up to present, in molecular solvents, most chemical reactions have been practiced in molecular solvents. For the last several decade, new class of solvent ionic liquids (ILs), has found out ILs have low melting point which is usually room temperature, so they call room temperature ionic liquids (Earle & Seddon, 2000; Kirchner, 2009) ILs or room temperature ionic liquids which, have been studied by a number of researchers are salts containing organic cations and (mostly) inorganic anions.

Furthermore, ILs (solvents) are more advantage than organic compounds (solvents)(see Table 1.1)(Sowmiah, Srinivasadesikan, Tseng & Chu, 2009). Therefore, industrial use of ILs began to replace organic compounds.

Table 1.1 Comparison of ionic liquids with organic solvents

Property	Organic solvents	Ionic liquids
Number of solvents	>1000	>1,000,000
Applicability	Single function	Multifunction
Catalytic ability	Rare	Common and tuneable
Chirality	Rare	Common and tuneable
Vapour pressure	Obeys the Clausius–Clapeyron equation	Negligible vapour pressure under normal conditions
Flammability	Usually flammable	Usually nonflammable
Solvation	Weakly solvating	Strongly solvating
Polarity	Conventional polarity concepts apply	Polarity concept questionable
Tuneability	Limited range of solvents available	Virtually unlimited range means “designer solvents”
Cost	Normally cheap	Typically between 2 and 100 times the cost of organic solvents
Recyclability	Green imperative	Economic imperative
Viscosity/cP	0.2–100	22–40,000
Density/g cm ⁻³	0.6–1.7	0.8–3.3
Refractive index	1.3–1.6	1.5–2.2

1.2.1 History

Since 1980s, the number of papers brought out on the ILs has grown almost exponentially (see Figure 1.6)(Sowmiah, Srinivasadesikan, Tseng & Chu, 2009; Zhang et al, 2009).

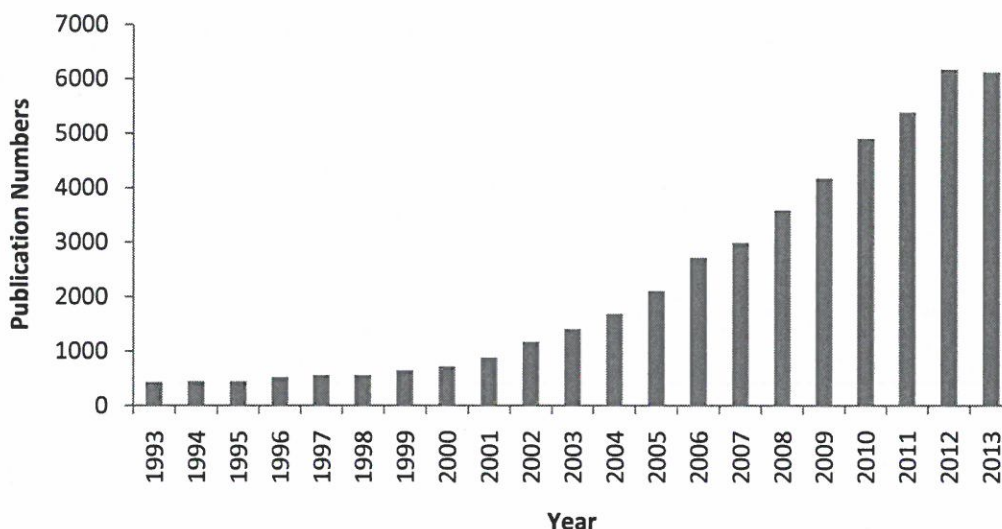


Figure 1.6 IL publications (on Dec30, 2013) determined from the ISI Web of Science in the last twenty years

Ethanol ammonium nitrate which is the first ILs was discovered in 1888 by S. Gabriel and J. Weiner (Gabriel & Weiner, 1888). In 1914, ethylammonium nitrate that has a melting point of 13-14 °C, was synthesized by Paul Walden. In the 1960s John Yoke studied that the mixtures of alkylammonium chlorides and copper(I) chloride were frequently liquids at Oregon State University. In the 1970s, Jerry Atwood discovered an extraordinary class of liquid salts he termed “liquid clathrates” at the University of Alabama. These consist of a salt combined with an aluminium alkyl. Then the aluminium alkyl formed an inclusion compound with one or more aromatic molecules. A formula for the ionic part is $M[Al_2(CH_3)_6X]$, where X is a halide and M is an inorganic or organic cation (Wasserscheid & Welton, 2008).

At the U.S. Air Force Academy, Major (Dr.) Lowell A. King and Richard Carlin studied on ILs in 1979, but they called 'room temperature molten salts'

In 1990, chloroaluminate ionic liquid was synthesized by Charles Hussey at Mississippi University.

The imidazolium-based chloro aluminate ionic liquid was synthesized in 1991 by Michael Zaworotko and he first made up a lot of the water-stable ionic liquids popular today (Wasserscheid & Welton, 2008). Since then, many of scientists have reported the synthesis of many ILS.

1.2.2 Structure of Ionic Liquids

They have a significantly lower symmetry. Moreover, both the charge of the cation and the charge of the anion are distributed over a greater volume of the molecule by resonance. As a result, the solidification of them will occur at lower temperatures. In some cases, particularly, if long aliphatic side chains are involved, a glass transition is observed instead of a melting point. (Kirchner, 2009)

The properties of ILs are encapsulated in Table 1.2 (Johnson, 2007; Stefanescu, Daly & Negulescu, 2012).

Table 1.2 The properties of ILs

A salt	Cation and or anion quite large
Freezing point	Preferably below 100°C
Liquidus range	Often >200°C
Thermal stability	Usually high
Viscosity	Normally <100 cP
Dielectric constant	Implied ≤ 30
Polarity	Moderate
Specific conductivity	Usually $<10 \text{ mScm}^{-1}$
Molar conductivity	$<10 \text{ Scm}^2 \text{ mol}^{-1}$
Electrochemical window	>2V ,even 4.5V except for Brønsted acidic systems
Solvent and /or catalyst	Excellent for a lot of organic reactions
Vapor pressure	Usually negligible
Non-flammable	
Acidic compositions are super acids	$\text{pK}_a \approx -20$

1.2.2.1 Cations

Normally, the ILS cation is an organic structure of low symmetry. The cationic centre many times includes a positively charged phosphorus or nitrogen which described insofar are based on

- Ammonium,
- Phosphonium,
- Sulphonium,
- Imidazolium,
- Pyridinium,
- Picolinium,
- Oxazolium,
- Pyrazolium,(see Figure 1.7) cations, usually completely substituted.

Recently, a lot of research has mostly concentrate on ILs consist of asymmetric dialkylimidazolium cations correlate with a variety of anions. Although the cations are modified, the feature of the ILs, especially

- The melting point
- Liquid range
- Solubility with other solvents
- Viscosity, can be altered (Kirchner, 2009) .

1.2.2.2 Anions

Anions that form ILs are usually weakly basic inorganic or organic compounds that have a diffuse or protected negative charge. Those compounds are alkyl sulphate, halide, tosylate (Chemfiles ,2005) etc (see Figure 1.7) (Kirchner, 2009).

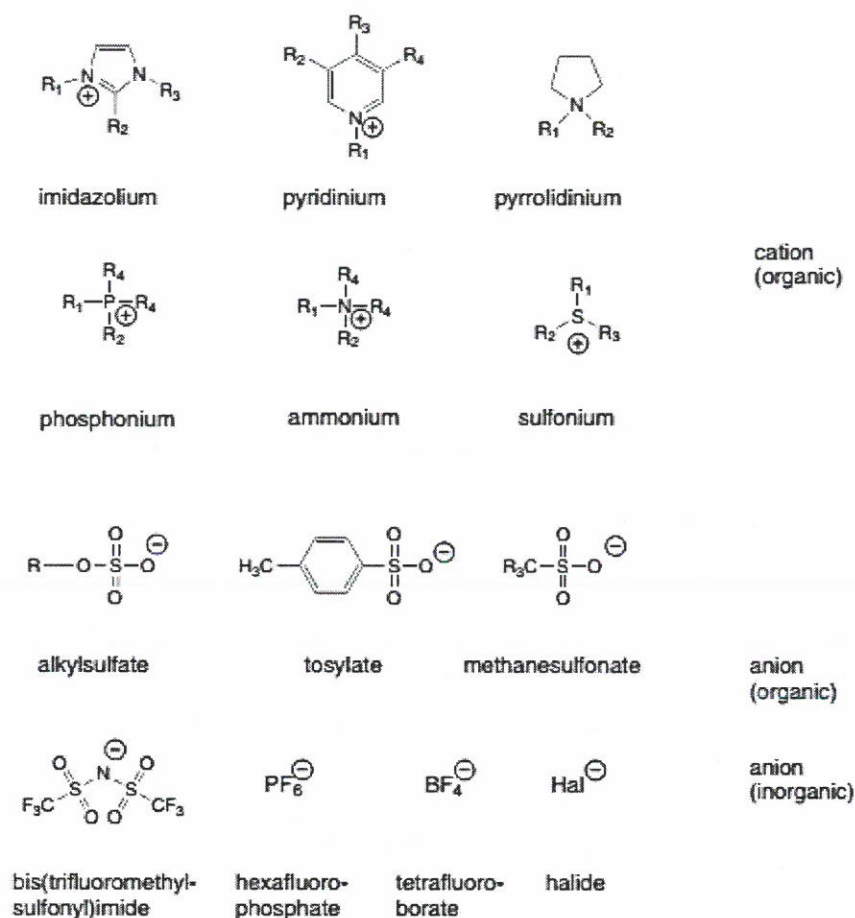


Figure 1.7 Mostly commonly anion and cation

1.2.3 Use and Applications of Ionic Liquids

The reason for the increase in number of studies can be ascribed to the unique features of these new materials. Eventually, the possible combinations of organic cations and anions places chemists in the position to design and fine-tune physical and chemical properties by introducing or combining structural motifs and, thereby, making tailor-made materials and solutions possible. The following chart summarizes important properties of ionic liquids and their potential and current applications (see Figure 1.8) (Chemfiles ,2005):

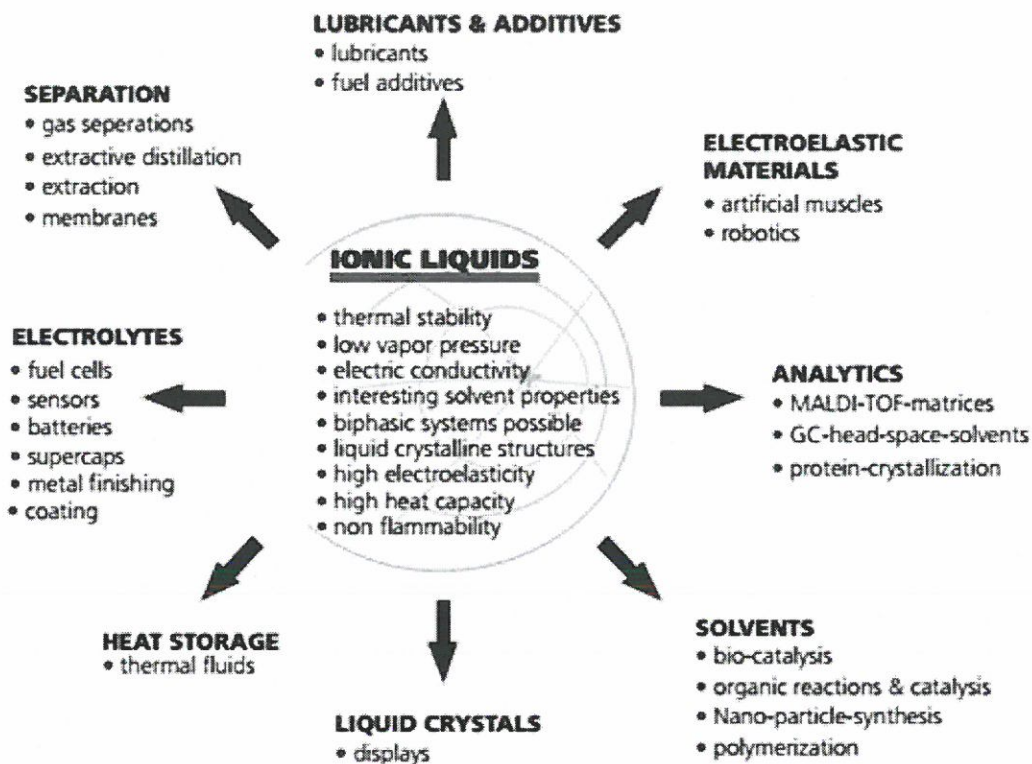


Figure 1.8 Applications of Ionic liquids

1.3 Graphene

1.3.1 Carbon Allotropes

There are a lot of different allotropes of carbon (C). The most important allotropes are graphite, which consists of sp^2 hybridized C atoms, and diamond, which consists of sp^3 hybridized C atoms (Ferrari & Robertson, 2000).

Diamond is a cubic structure in which each C atom is linked to four other C atoms by sp^3 bonds in a tetrahedral array and is transparent. A diamond structure is shown in Figure 1.9 (Wikimedia Commons, 2009).

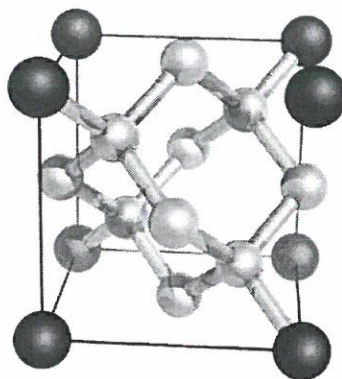


Figure 1.9 Diamond structure

Natural graphite is abundant in the world. Unlike diamond, the structure of graphite is notably anisotropic, and this feature has influence upon its physical properties. Graphite has three stacking types, which are AAA stacking, ABAB(Hexagonal) stacking and ABCABC(Rhombohedral) ABAB and ABCABC structures are shown in Figure1.10 (Pierson, 1993).

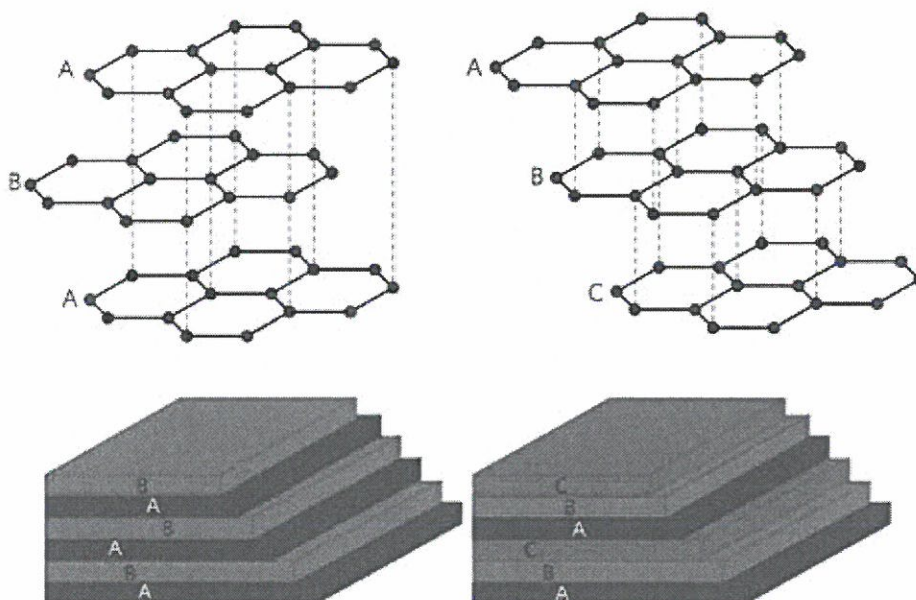


Figure 1.10 Graphite structures (Nature ,2010)

Different properties of carbon allotropes is shown in Table 1.2 for a better comparison (Burchell, 1999).

Table 1.3 Some properties of carbon allotropes

Property	Diamond	Graphite
Crystal structure	Tetrahedral	Hexagonal and Rhombohedral
Density (g/cm ³)	3.51	2.26
Hybrid type of C atom	sp ³	sp ²
C-C Bond Length (Å)	1.54	1.42
Young's Modulus (GPa)	1063	1020
Thermal Conductivity (W/mK)	2200	25-470
Melting Point (K)	4500	4450

There are different geometries of graphitic materials, which compose of graphene that is a sheet of two-dimensional (2D) single layer sp² hybridized carbon atoms. These materials are fullerenes, carbon nanotubes and graphite. Fullerenes which consist of sixty C atoms is spherical structures and zero-dimensional(0D). Carbon nanotubes can be made by slicing and rolling graphene sheets and is one-dimensional (1D). Graphite is stacked into graphene and three-dimensional (3D) layered structures. Different geometries of graphene are shown in Figure 1.11 (Liu, Cui & Losic, 2013).

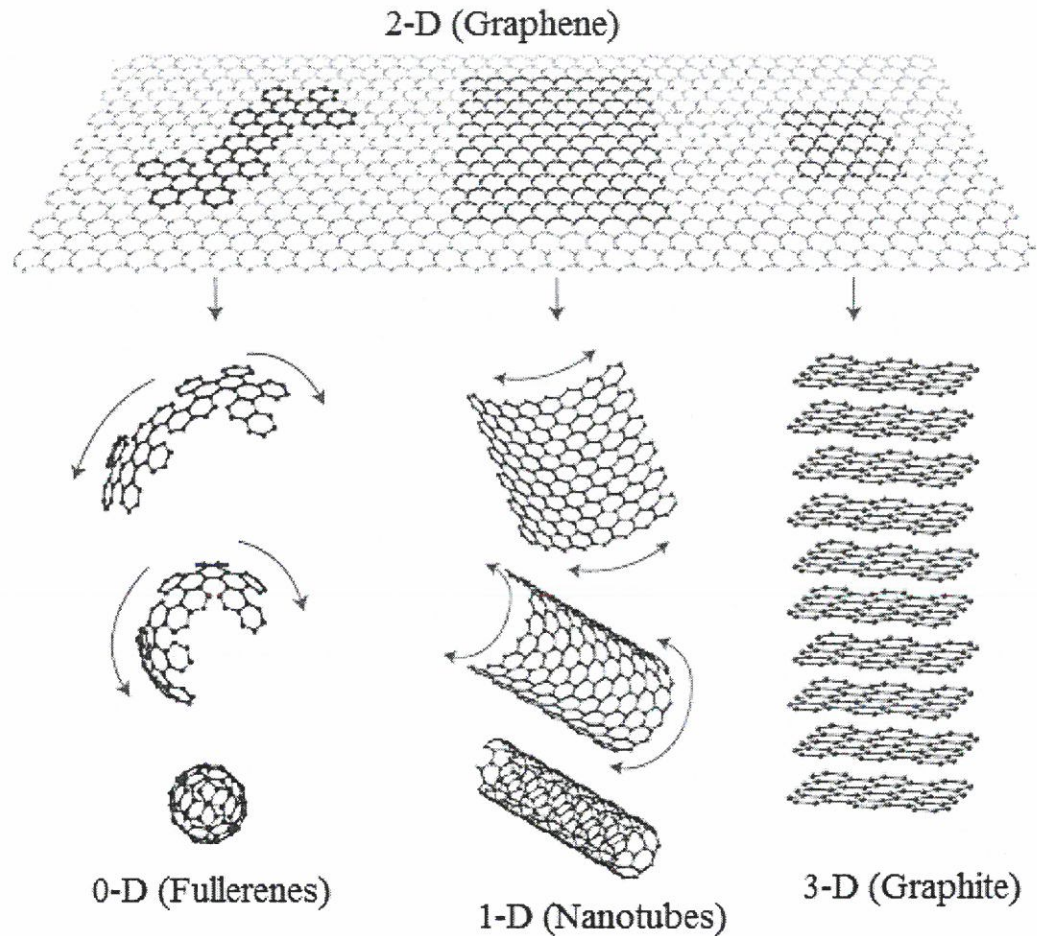


Figure 1.11 Mother of all graphitic forms. Graphene is a 2-D building material for carbon materials with other dimensions including zero dimensions (fullerenes), one dimension (carbon nanotubes) and three dimensions (graphite)

1.3.2 Properties of Graphene

Since 2004, a lot of interesting properties of graphene have been discovered, which include high thermal conductivity, large theoretical specific surface area, high charge carrier mobility, and excellent mechanical properties. Properties of graphene and carbon nanotubes are shown in Table 1.4 (Liu, Cui & Losic, 2013; Goenka, Sant & Sant, 2014).

Table 1.4 Properties of graphene and carbon nanotube

Property	Graphene	Carbon Nanotube
Young's Modulus (GPa)	1000-1100	960
Fracture Strength (GPa)	130	10-60
Optical Transmittance (%)	97.7	
Charge carrier Concentration (cm ⁻²)	1.4x10 ¹³	
Room temperature mobility (cm ² V ⁻¹ s ⁻¹)	~200.000	100.000
Thermal Conductivity (W/mK)	~5000	~3000~3500
Electrical Conductivity (S/cm)	10 ⁴	106

1.4 Cellulose

Cellulose (C₆H₁₀O₅)_n is one of the most important organic polymers in the world and is a biodegradable, biocompatible and almost inexhaustible source of raw materials with environmentally friendly (Kunchornsup & Sirivat, 2010; Mahmoudian, Wahit, Imran, Ismail & Balakrishnan, 2012) (see Figure 1.12). Cellulose, which consists of a linear β-(1→4) linked glucose repeating units, has been considerably used for industrial domains such as paper polymer, textile, fiber and food industries.

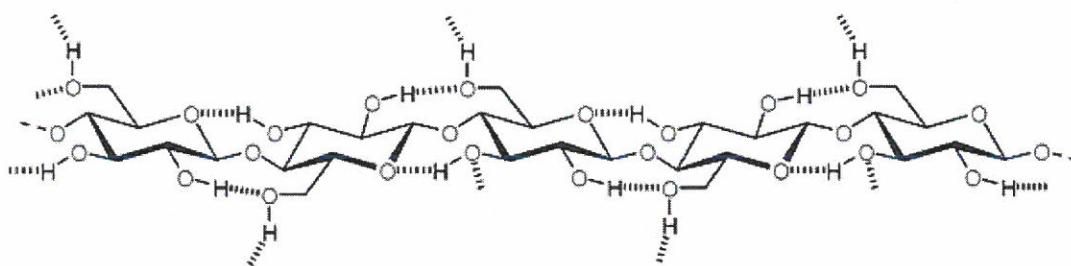


Figure 1.12 The structure of cellulose(Vitz, Erdmenger, Haensch & Schubert, 2009)

One of the major objection of cellulose concerning its industrial application is the insolubility widespread solvents due to its fibril structure and the pronounced presence of intra- and intermolecular hydrogen bonds. (Vitz, Erdmenger, Haensch & Schubert, 2009). Therefore, it is dissolved in direct solvent (such as N-methyl-

morpholineN-oxide (NMMO) monohydrate (Wendler, Todi & Meister, 2012), LiCl/DMAc, calcium thiocyanate, 8% NaOH–water or ionic liquid, regenerated (or coagulated) in a non-solvent (alcohols, water) and then dried in a special way that prevents pores collapse, i.e. either via freeze-drying, or under CO₂ supercritical conditions (Sescousse, Gavillon & Budtova, 2011).

Recently, as one of its new research, cellulose paper has been discovered as a smart material which can be used as actuators and sensors. The smart material is called cellulose electro active paper. If an electric field was implemented on paper, a high displacement with low force was generated (Kim, 2007; Kim & Cai, 2012). There are a lot of advantages of cellulose electro active paper which are

- Light weight
- Dryness
- Biodegradability
- Abundance
- Low price
- Large displacement
- Low actuation

On the other hand, this material has much sensitive to humidity its maximum bending performance was displayed at high humidity conditions, and its performance is reduced with time (Kim & Cai, 2012).

1.4.1 The Dissolution Mechanism of Cellulose in 1-n-Butyl-3-Methylimidazolium chloride

Cellulose dissolving mechanism involves the hydrogen and oxygen atoms of cellulose-OH in the composition of electron acceptor–electron donor complexes which interact with the IL. Those interaction, the cellulose atoms attend as electron pair donor and hydrogen atoms act as an electron acceptor (see Figure 1.13) (Zadegan, Hossainipour, Ghassai, Rezaie & Naimi-Jamal, 2010).

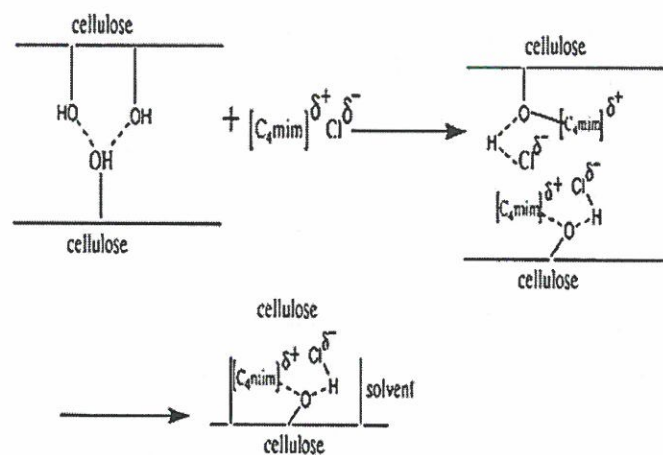


Figure 1.13 Dissolution of cellulose in ionic liquids ($[C_4mim]^+ Cl^-$ and BMIMCl)

CHAPTER TWO

EXPERIMENTAL METHOD AND INSTRUMENTATION

2.1 Material

Cellulose microcrystalline powder (Cel) (C435236-250G) was supplied from Sigma-Aldrich Corp. Butyl methyl imidazolium chloride (see Figure 2.1 a), was used as ionic liquid and abbreviated as BmimCl. N,N-dimethylacetamide(see Figure 2.1 b) (DMAC) was used as plasticizer in this study. These two chemicals were purchased from Sigma-Aldrich Corp. Graphene(Gr) was obtained from Grafen Kimya Sanayi A.Ş with an average particle diameter of 50-100 nm and thickness of approximately 5–10 μm .

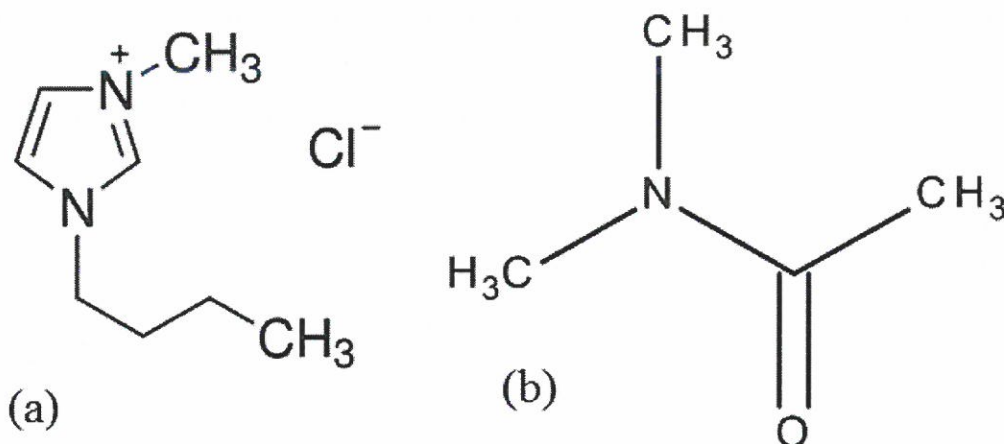


Figure 2.1 Schematic representation of the structures of BmimCl(a) (Sigmaaldrich ,2013) and DMAC(b) (Merck ,2014)

2.2 Fabrications of Cel-Cl-DMAC and Cel-Cl-DMAC-Gr

6.45 g BmimCl was melted by heating. 0.969 g Cel was added to molten ionic liquid and the mixture was subjected to stirring until a homogeneous liquid solution was formed. After dissolution of cellulose, 4.5 mL of DMAC was added to this mixture. Gr particles with fractions of 0.1, 0.25, 0.375 and 0.5 wt% of total mass material were dispersed in the solution using an ultrasonic homogenizer (UP400S-Hielscher) (20 A% with 1 cycle for 1 min. and 50 A% with 1 cycle for 2 min). Degassing the solution in a vacuum oven for 12 h at room temperature, it was casted on a glass plate with thickness of about 1 mm with film casting knife (see figure 2.2 b). Different Gr loaded films are shown in Figure 2.3 .

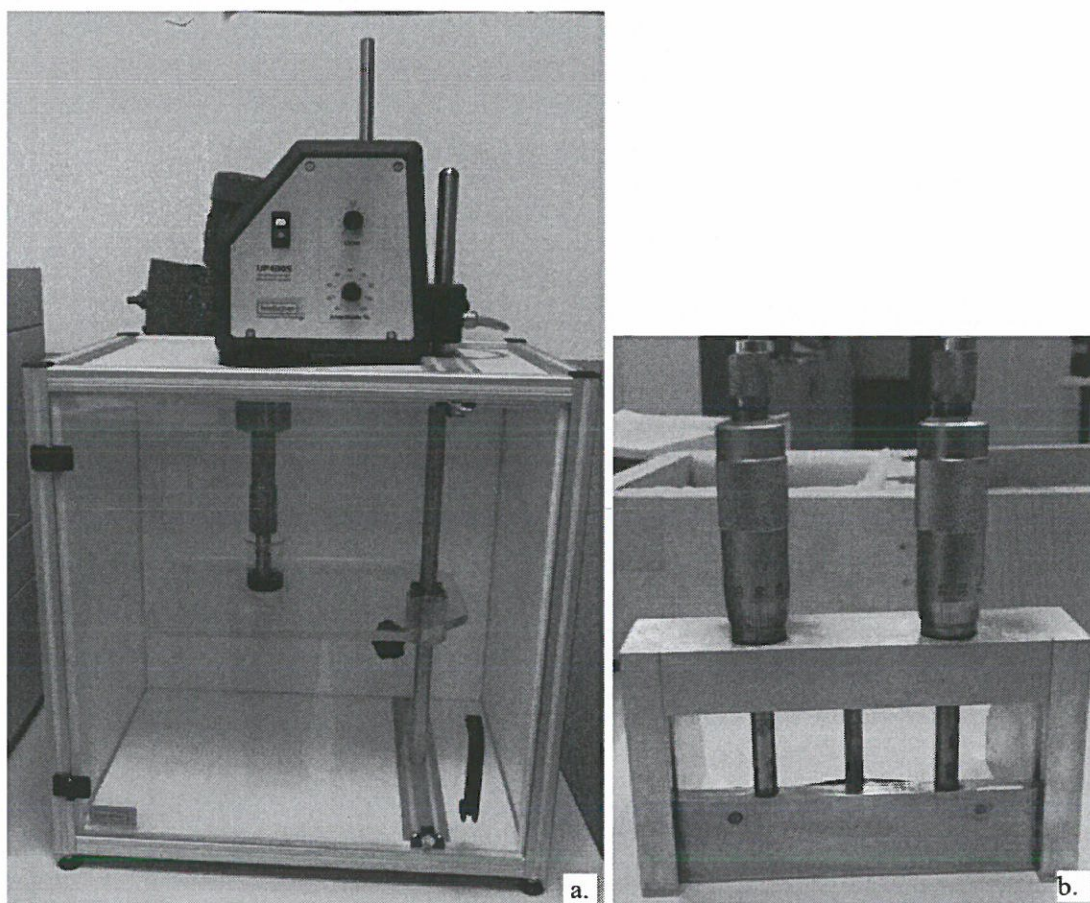


Figure 2.2(a) Ultrasonic processor (b) Film casting knife

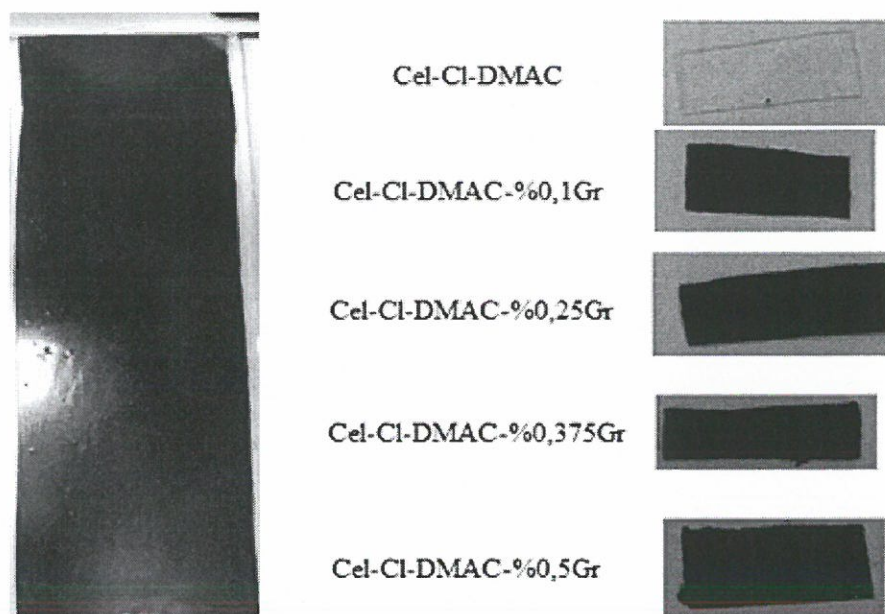


Figure 2.3 Different Gr loaded films

2.3 FTIR Analysis

A FTIR spectrophotometer (Perkin Elmer BX-II) was used for the entire study. 1g of samples was ground into powder and mixed with infrared-grade KBr powder (100 mg) and pressed into a pellet for measurement. Each spectrum was recorded in the range of $400\text{--}4000\text{ cm}^{-1}$, with a resolution of 2 cm^{-1} . The background spectrum of KBr pellet was subtracted from the sample spectra.

2.4 Thermogravimetric Analysis (TGA)

Thermogravimetric analyses of the samples were conducted by using TGA (Perkin Elmer TGA) at a heating rate of $10\text{ }^{\circ}\text{C}/\text{min}$ under nitrogen atmosphere. For BmimCl, the analysis was conducted from 30 to 400°C . For the other samples, the analyses were conducted in the range $30\text{--}600\text{ }^{\circ}\text{C}$.

2.5 X-Ray Diffraction (XRD) Analysis

X-ray diffraction (XRD) patterns of graphene (Gr), cellulose, Cel-Cl-DMAC and Gr- loaded Cel-Cl-DMAC composites were obtained by using Philips X-Pert Pro Diffractometer using Ni-filtered $\text{Cu K}\alpha$ radiation ($\lambda = 1.54\text{ \AA}$) operated at 45 kV and

40 mA. The data were collected in 2θ angle ranged from 5° to 80° . The scan step size and time per step were set to 0.03° and 10 s, respectively.

To calculate the crystallinity index (CI) of cellulose from the XRD patterns we used the Segal's equation. The crystallinity index of cellulose was calculated from the ratio of the height of the 002 peak (I_{002}) and the height of the minimum (I_{AM}) between the 15.7 and the 22.8 peaks, as shown in Figure 3.10

$$CI = \frac{I_{002} - I_{AM}}{I_{002}} \quad (2.1)$$

Crystallite size was calculated using Scherrer's formula (Seki, Sarikanat, Sever & Durmuşkahya, 2013):

$$L = \frac{K\lambda}{B \cos \theta} \quad (2.2)$$

where $K = 0.89$ is Scherrer's constant, B is the full width at half maximum (rad) and k the wavelength of the radiation.

2.6 Scanning Electron Microscope (SEM) Observations

The surface morphologies of samples were investigated through scanning electron microscope (FEI Quanta FEG 250). Observations were conducted at an accelerating voltage of 4 kV.

2.7 Mechanical Properties

The tensile strength, Young modulus and elongation at break values were obtained by a tensile testing machine with a 100N load cell at a crosshead speed of 0.1 mm/min. The sample size was about 10x40 mm.

2.8 Electrical Properties

Surface Resistance of cellulose-based films were determined by using two-probe setup, which is connected to Keithley 2612 System SourceMeter. For all the measurements, the distance between two probes was adjusted to 2mm.

2.9 Electroactive Properties

2.9.1 Experimental Setup

In order to monitor the tip displacement of actuators in case of various electrical stimuli, a computer based experimental setup is developed (see Figure 2.4). The experimental setup is made up of two sub systems: an electrical actuation system and a vision system both of which work on standalone NIPXIe-9133pc.

The electrical actuation system is made up of a data acquisition card (NI-PXI 7854R) to create user defined signal form. The output of the data acquisition card is applied to actuator through a buffer (TDA2040) Op amp circuit. The vision system is a single camera (Basler acA2040-180km camera and Computar M0814-MP - 8mm – F1.4 lens) connected to a frame grabber (NI PXIe-1435). The user interface for control of the experimental setup is developed in LabView.

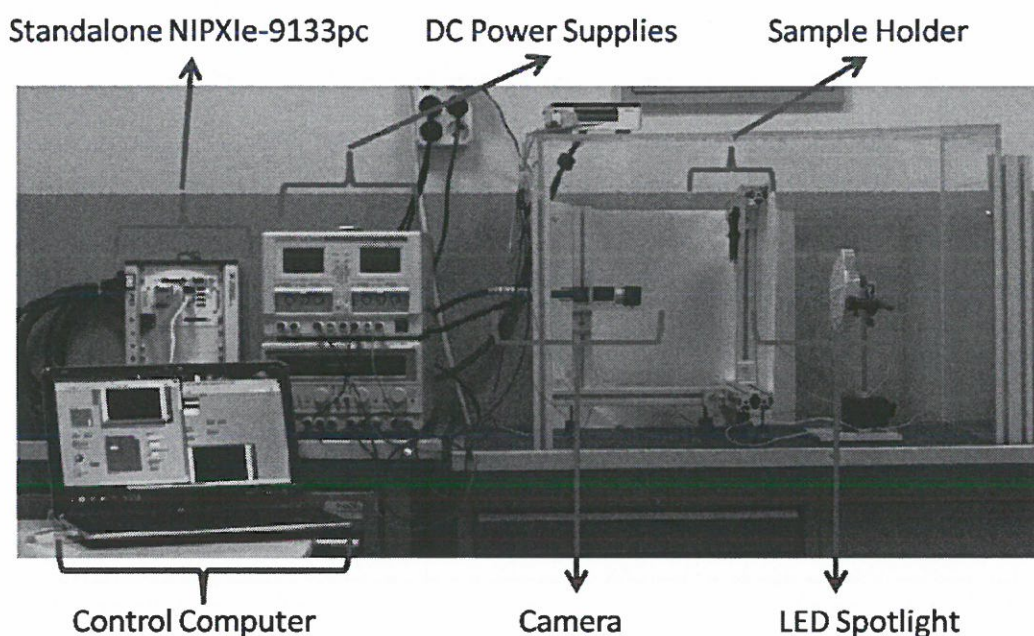


Figure 2.4 The experimental setup for measuring actuation of IPMC actuator

The two subsystems are synchronized to enable accurate data collection in time scale. A vision setup for data collection is used to follow exact tip position of the sample since the IPMC actuators change their curvature when excited and thus tip displacement takes place on a curve on the plane. Therefore, using a laser displacement measurement system, which measures only linear tip displacements, may lead to errors. The vision system is calibrated by the help of a calibration sample with known dimension placed in the measurement plane (see Figure 2.5). A scale for image plane to real world coordinates is defined using the calibration results.

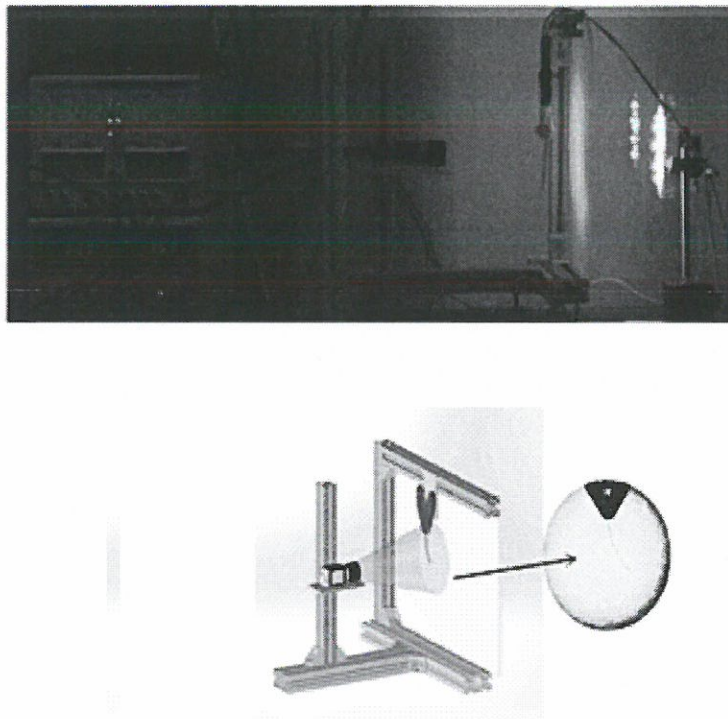


Figure 2.5 The vision system for measuring actuation of IPMC actuator

2.9.2 Fabrication of IPMC Actuators

Figure 2.6 shows fabrication methods of Cel-Cl-DMAC and Gr-loaded Cel-Cl-DMAC/Gold film for IPMC actuators.

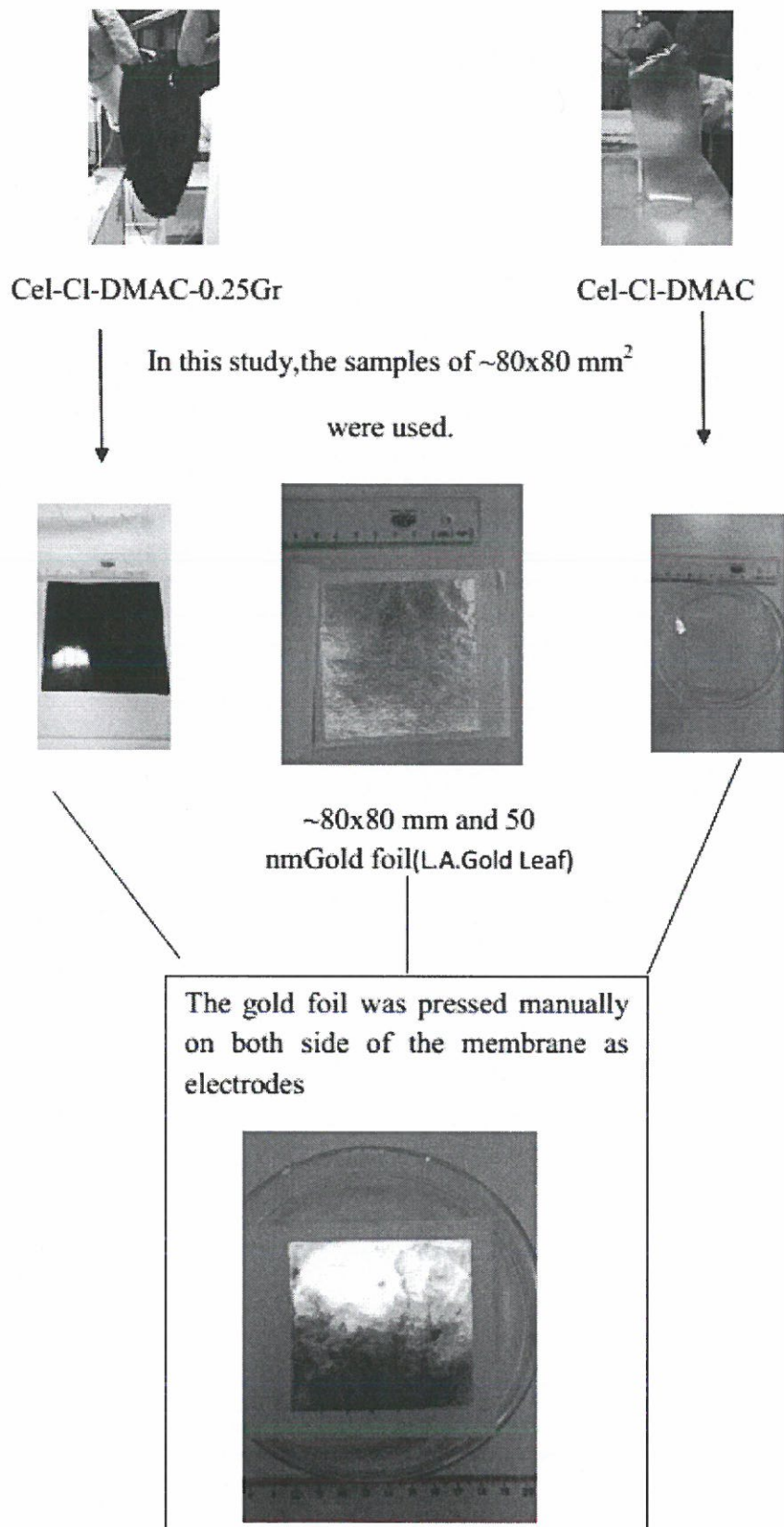


Figure 2.6 Production of IPMC actuators

2.9.3 Experiments

The aim of this experiment is to determine the effect of Gr loading on actuator performance of Cel-Cl-DMAC films. The sample sizes (Cel-Cl-DMAC with Gr loaded Cel-Cl-DMAC) were presented in Figure 2.7.

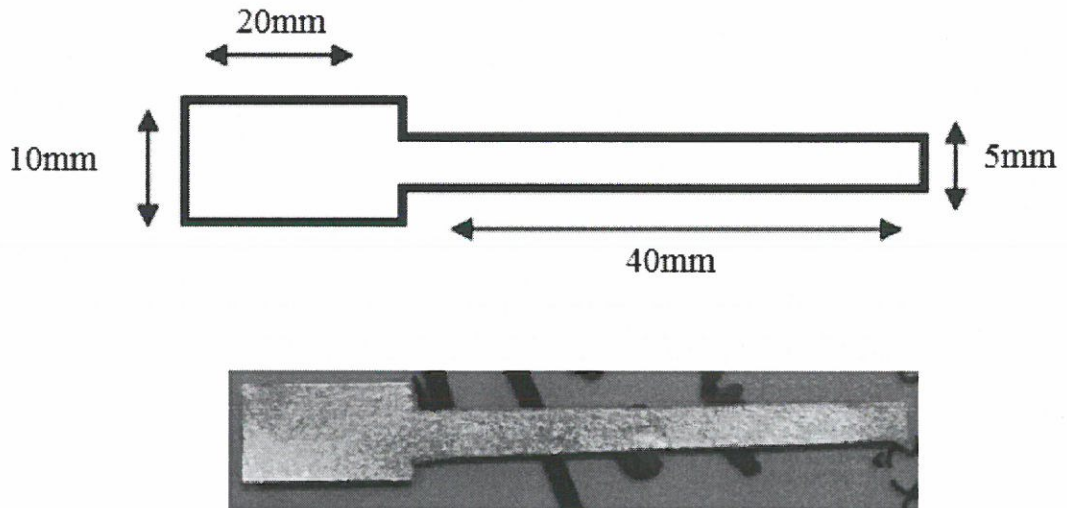


Figure 2.7 Actuators samples

This set of examples uses DC excitation under 3, 5 and 7 V. The objective of DC experiments is to obtain transient response characteristics and quasi-steady state value of the actuators.

CHAPTER THREE

RESULTS AND DISCUSSIONS

3.1 FTIR Analysis

Figure 3.1 shows the spectra of the Cel and graphene loaded Cel-Cl-DMAC. Table 3.1 shows the main absorption bands for the studied samples. As can be seen from Table 3.1, the band in the range 3200–3700 cm^{-1} is assigned to the hydrogen-bonded OH stretching vibration. The bands between 2850 and 2970 cm^{-1} are attributed to the CH and CH₂ stretching modes. The band at 1633 cm^{-1} is owing to the bending mode of the absorbed water. Besides, the bands in the region 1250–1450 cm^{-1} correspond to C–O–H and C–H bending modes. The bands in the region 950–1250 cm^{-1} are due to C–O stretching modes.

Table 3.1 The main absorption bands for the samples

Bands Wavenumber(cm^{-1})	Assignment
3200-3700	OH stretching
2850-2970	CH and CH ₂ stretching
1647	Absorbed water 'bending' vibration
1250-1450	C–O–H and C–H bending
950-1250	C–O stretching

Figure 3.1a shows FTIR spectrum of cellulose. Similar characteristic bands related to the cellulose were found by Oh et al.,(2005)., Li et al. ,(2009). and Agarwal et al.,(2011) .

It is known that, in order to dissolve cellulose, many intra- and inter- molecular hydrogen bonds are required. After dissolution of cellulose in ionic liquid (BmimCl) and DMAC, small changes were observed. For example an absorption band at 1539 cm^{-1} was observed due to the stretching vibration of C=O groups, which indicates the presence of acetamide component (Geng et al., 2011). Besides, a new absorption band appears in the region 2968-3145 cm^{-1} because of CH and CH₂ stretching vibrations after dissolution process. As can be seen from Figure 3.1 b, c, d, e and f, small shifts were seen in the spectra after Gr loading to the mixture. It is interesting to note that after 0.5% Gr was added to the mixture, the absorption bands cannot be seen clearly due to matrix effect of Graphene. A similar result was obtained for the

sample of Cel-Cl-DMAC-0.25Gr. The band at 1639 cm^{-1} in the spectrum of Cel-Cl-DMAC cannot be seen after 0.25% Gr was added to the mixture.

The hydrogen-bonded OH stretching mode at 3428 cm^{-1} , in the spectrum of Cel-Cl-DMAC, changed to lower wave number, 3417 cm^{-1} , after 0.1% Gr was added to the mixture. The position of bands in the range $2800\text{-}3500\text{ cm}^{-1}$ for the samples of Cel-Cl-DMAC-0.1Gr and Cel-Cl-DMAC-0.375Gr was obtained to be the same. This difference in spectra of samples containing various amounts of Graphene may be attributed to inhomogeneous distribution of graphene in the mixture.

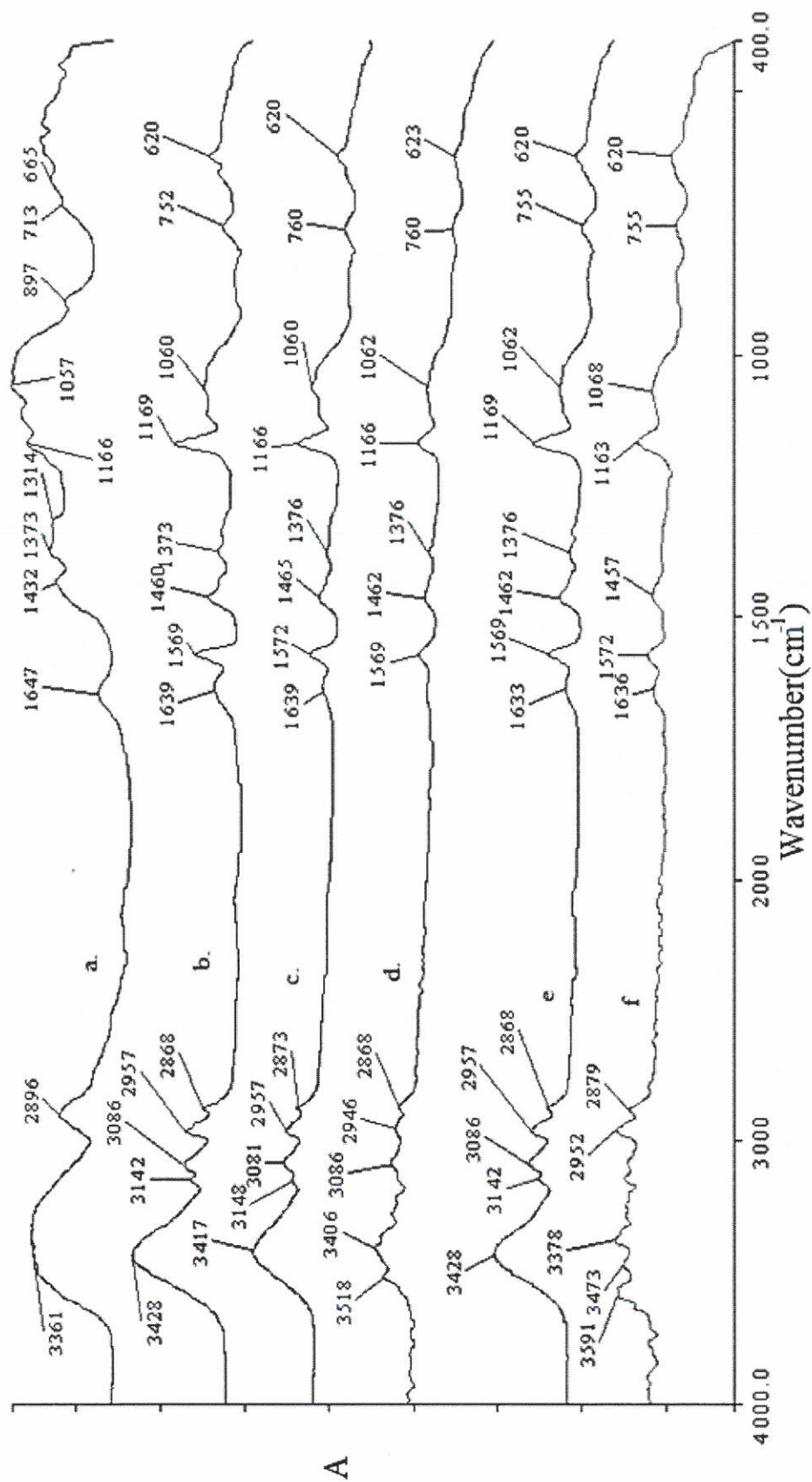


Figure 3.1 FTIR spectra of samples: a)cellulose, b) Cel-Cl-DMAC, c) Cel-Cl-DMAC-%0.1Gr, d) Cel-Cl-DMAC-%0.25Gr, e) Cel-Cl-DMAC-%0.375Gr, f) Cel-Cl-DMAC-%0.5Gr

3.2 Thermogravimetric Analysis (TGA)

TGA profiles for BmimCl, cellulose, Cel-Cl-DMAC film and Gr loaded Cel-Cl-DMAC samples are given in Figure.3.2-3.8. The involved TGA data were summed up in Table 3.2. According to the data in table 3.2, the thermal degradation of BmimCl, Cel, Cel-Cl-DMAC and Gr loaded Cel-Cl-DMAC is divided into two stages, one small and one main stage. It is known that in dissolution mechanism of cellulose in BmimCl, cellulose is attracted by Cl^- during the dissolving process in BmimCl, and part of the molecular cellulose chain and many of the hydrogen bonds are reduced, resulting in a decrease in molecular weight and thermal stability (Chen, Wang & Liu, 2012). According to the Figure 3.2, the initial degradation, the main maximum degradation, and the final degradation rate temperatures for BmimCl was obtained to be 216, 293, and 336°C, respectively. As can be seen in Figure 3.4, the main maximum degradation rate temperature for Cel and Cel-Cl-DMAC was 339 and 289°C, respectively. After film formation of cellulose with the dissolution in BmimCl, maximum decomposition temperature diminished by 50°C. After graphene loading to the mixture, maximum and initial decomposition temperatures of Cel-Cl-DMAC decreased slightly. However final decomposition temperature decreased considerably (from 353°C for Cel-Cl-DMAC to 318°C for Cel-Cl-DMAC-Gr-0.375), that is, 35°C diminishment was observed. It can be noted that after graphene loading to Cel-Cl-DMAC, thermal stability of Cel-Cl-DMAC decreased slightly.

In addition, the TGA curves of the samples also showed weight losses of 6.7% and 5.2-12.3% up to 100°C for Cel-Cl-DMAC and Graphene-loaded Cel-Cl-DMAC, respectively, which was ascribed to evaporation of water. It is reported that the gel formation takes gradually place with absorption of water and simultaneously exclusion of the excess ionic liquids (Takegawa, Murakami, Kaneko & Kadokawa, 2010). The gel material is consisted of cellulose, BmimCl, and water and obtained by the formation of non-crystalline aggregates in solution by gradually absorbing water (Kadokawa, Murakami & Kaneko, 2008).

As shown in Table 3.2, thermal decomposition residues (nonvolatile carbonaceous material) of Cel-Cl-DMAC is 5.8%. However after graphene loading to Cel-Cl-DMAC the amount of nonvolatile carbonaceous material decreased. This may be due

to the weak interaction of graphene nano-structures with cellulose material and/or inhomogeneous dispersion of graphene into Cel-Cl-DMAC mixture.

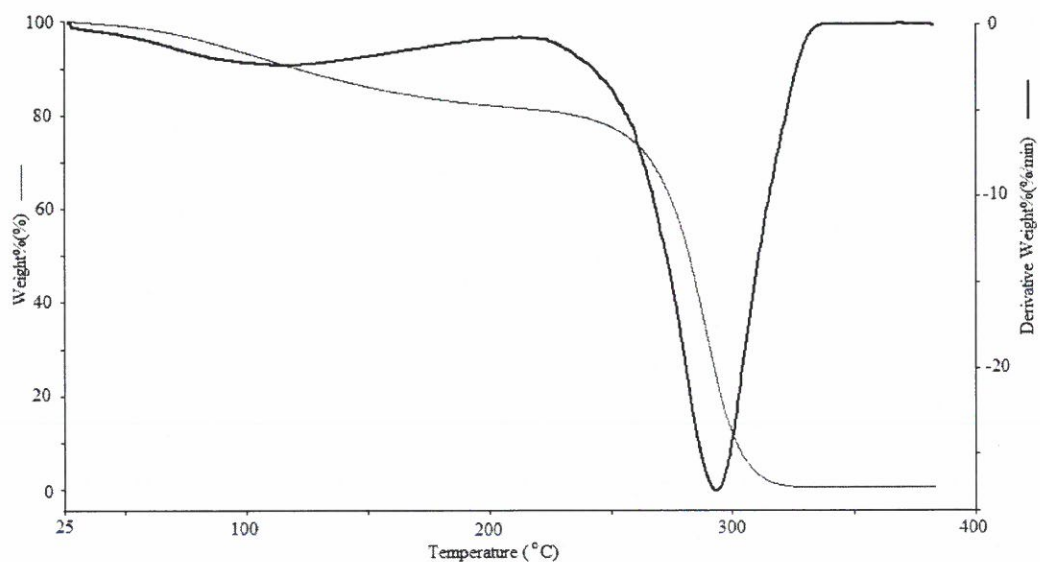


Figure 3.2 TGA profile for the BmimCl

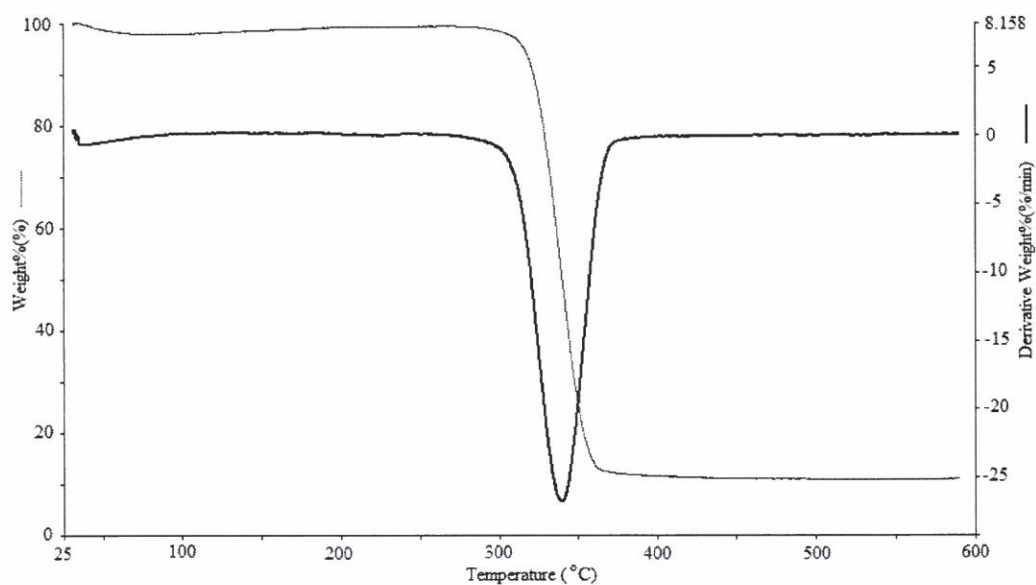


Figure 3.3 TGA profile for the cellulose

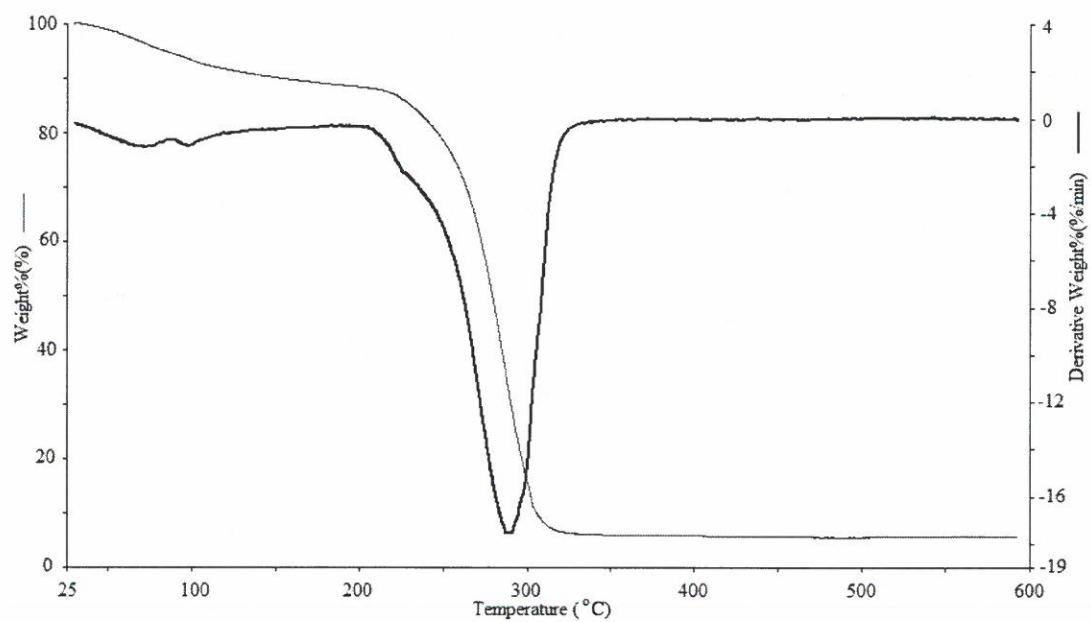


Figure 3.4 TGA profile for the Cel-Cl-DMAC

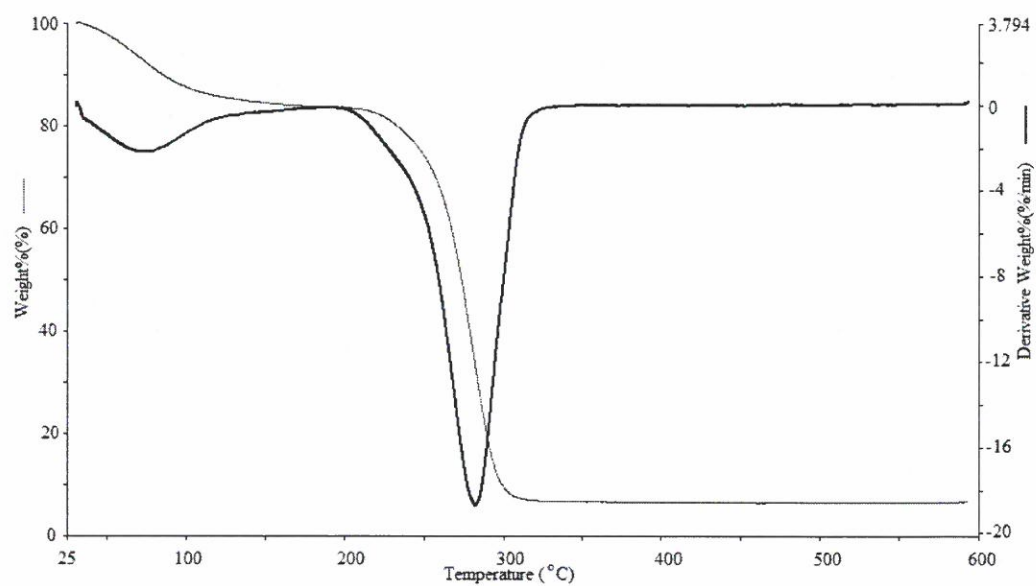


Figure 3.5 TGA profile for the Cel-Cl-DMAC-0.1Gr

Table 3.2 TGA data for the samples

Samples	Mass loss to 25-100°C	Mass loss to 25-600°C	1 st stage (°C)	Initial decomposition temperature (°C)	Maximum decomposition temperature (°C)	Final decomposition temperature (°C)
BmimCl	8.2	99.1	120	216	293	336
Cellulose	1.9	88.9	32	276	339	403
Cel-Cl-DMAC	6.7	94.2	67 and 96	198	289	353
Cel-Cl-DMAC-0.1Gr	12.3	93.2	74	203	283	336
Cel-Cl-DMAC-0.25Gr	11.3	90.6	57	203	281	323
Cel-Cl-DMAC-0.375Gr	5.2	87.7	64	200	278	318
Cel-Cl-DMAC-0.5Gr	8.9	90.5	69	201	280	332

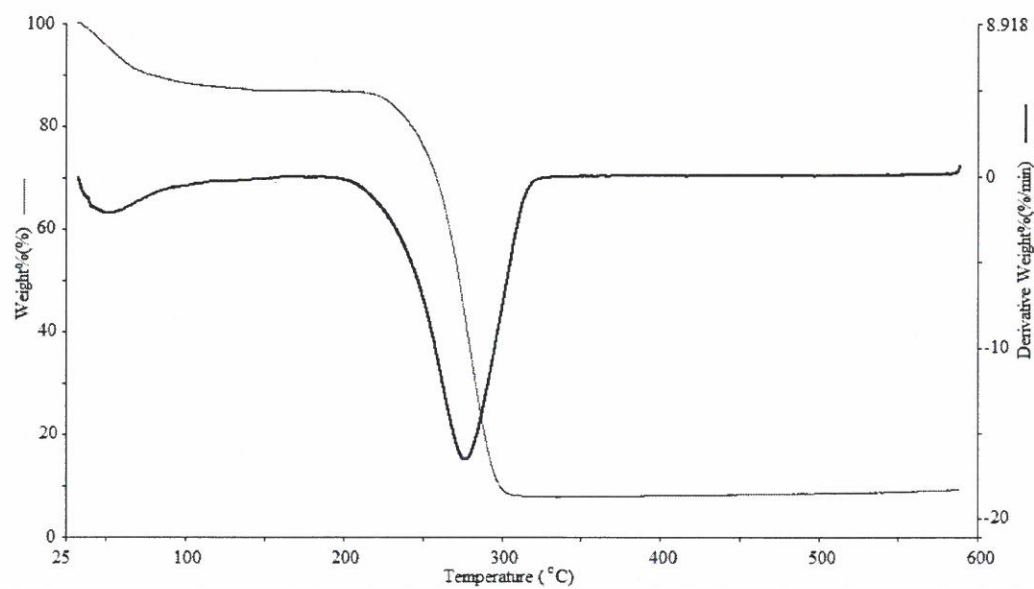


Figure 3.6 TGA profile for the Cel-Cl-DMAC-0.25Gr

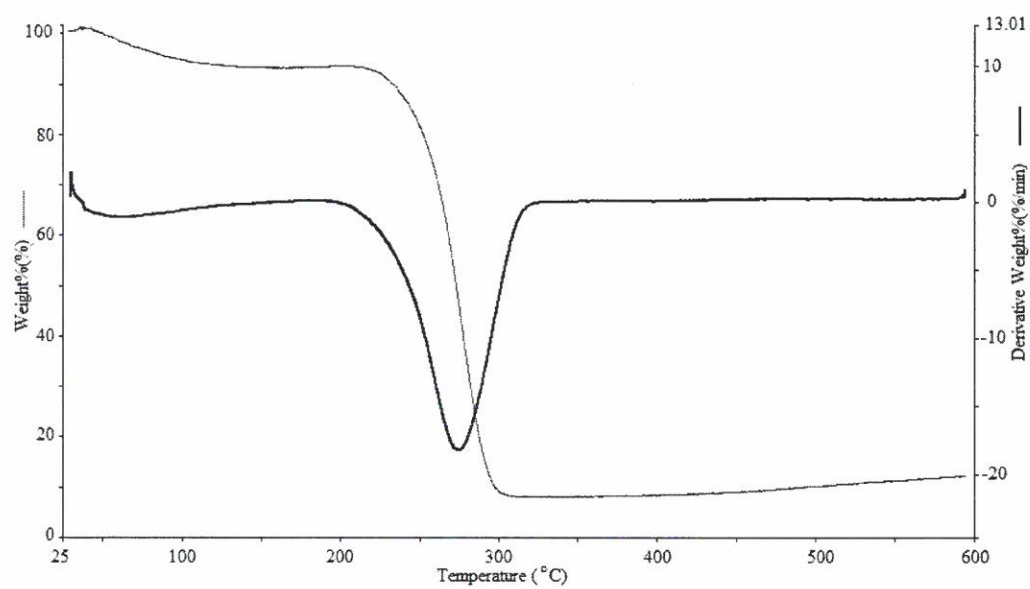


Figure 3.7 TGA profile for the Cel-Cl-DMAC-0.375Gr

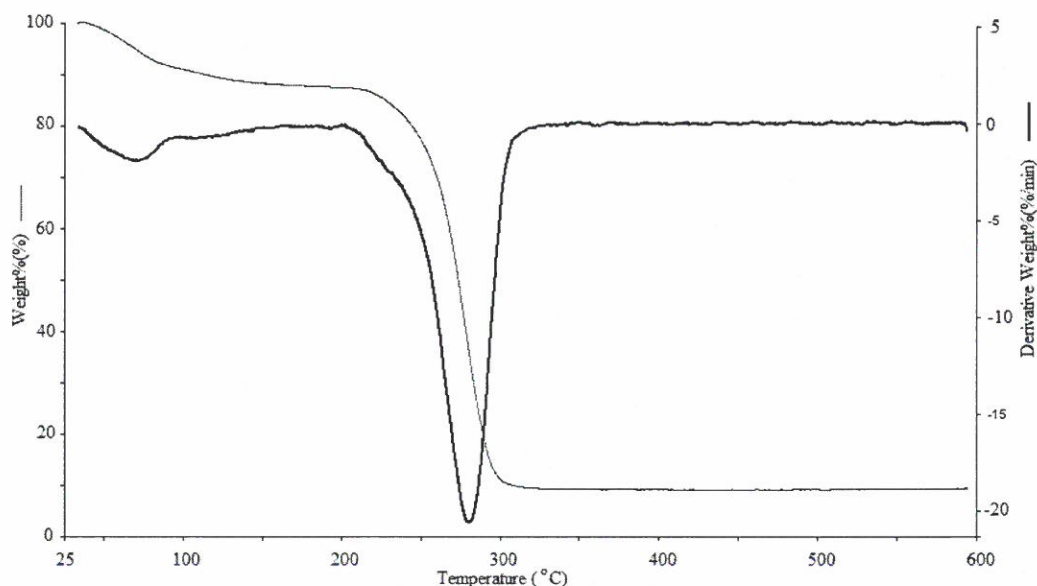


Figure 3.8 TGA profile for the Cel-Cl-DMAC-0.5Gr

3.3 X-Ray Diffraction (XRD) Analysis

X-ray diffractogram of Gr is presented in Figure 3.9. The XRD profile of Gr shows two diffraction peaks at $2\theta=26.5^\circ$ and 54.5° . Gr demonstrated an intense peak at 2θ value of $\sim 26.5^\circ$, corresponds to the stacking of the single graphene layers (Chieng, Ibrahim, Wan Yunus, Hussein & Silverajah, 2012). The XRD pattern of cellulose is given in Figure 3.10. XRD pattern of cellulose exhibited three diffraction peaks at 2θ angles of 15.7° , 22.8° and 34.7° . The peak at 2θ angle of 22.8° originates from the cellulose crystalline plane 002. Similar characteristic peaks related to the cellulose were also found by Zadegan et al, (2011) and Stefanescu et al, (2012).

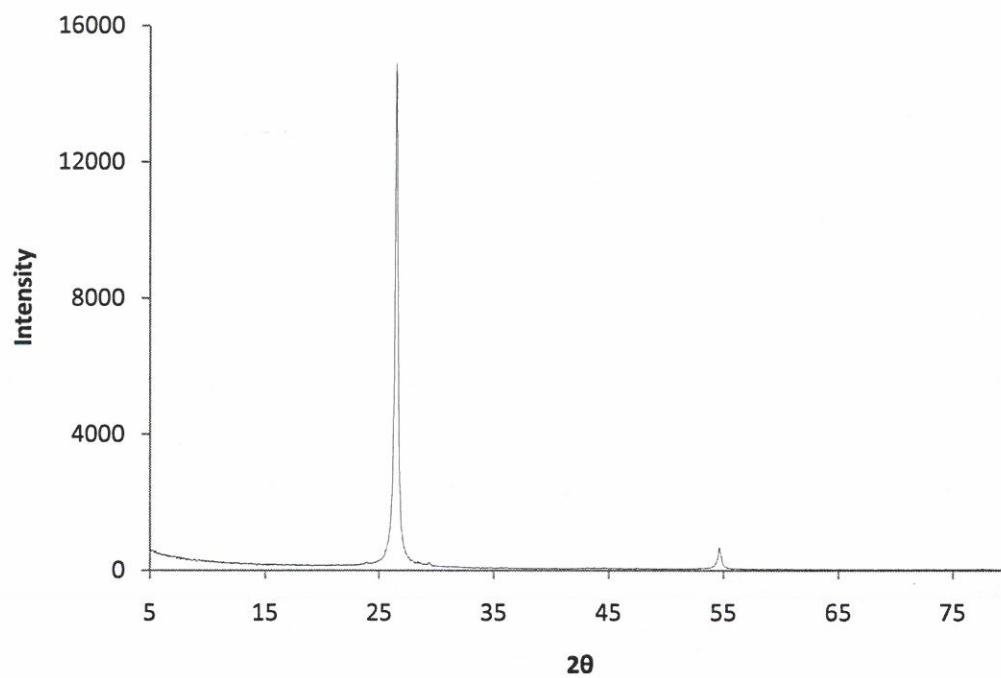


Figure 3.9 X-ray diffraction pattern of graphene

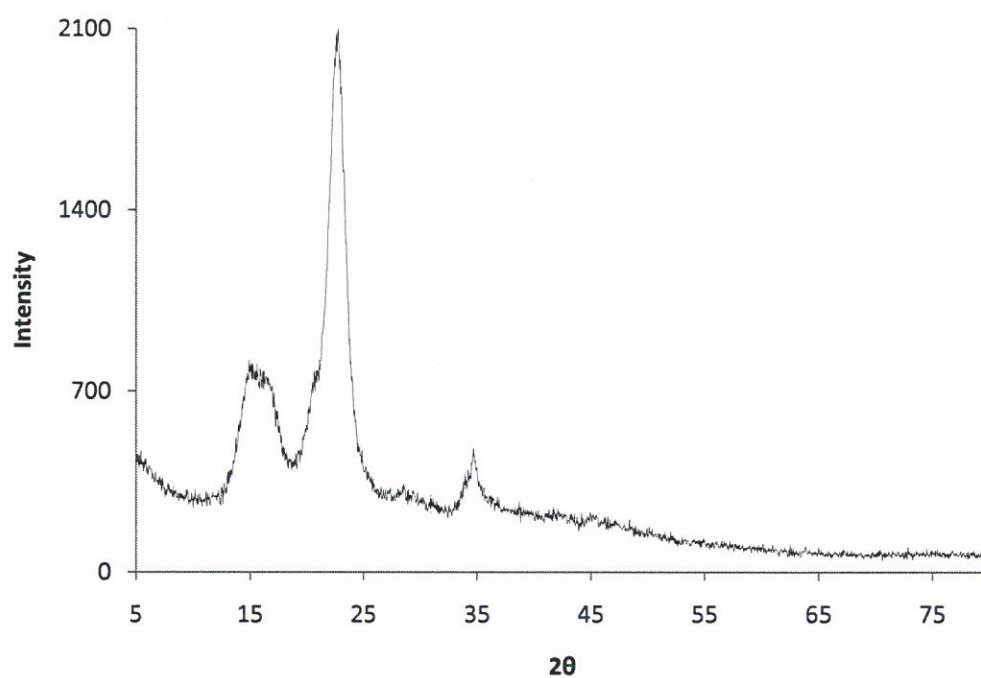


Figure 3.10 X-ray diffraction pattern of cellulose

XRD pattern of Cel-Cl-DMAC film is shown in Figure 3.12. After dissolution of cellulose in BmimCl and DMAC, some changes were observed. The main characteristic peak of cellulose is also observed in the XRD pattern of Cel-Cl-DMAC film. Film formation makes the peak at 2θ angle of 22.8° wider, leading to it to become less resolved. Besides, the first and third peak of cellulose was disappeared. XRD patterns of Cel-Cl-DMAC-0.1Gr, Cel-Cl-DMAC-0.25Gr, Cel-Cl-DMAC-0.375Gr, and Cel-Cl-DMAC-0.5Gr are presented in Figures 3.13, 3.14, 3.15 and 3.16, respectively. When Gr was loaded into Cel-Cl-DMAC, both the basic characteristic peak at 2θ angle and the peak intensity slightly changed. The peak which belongs to graphene cannot be seen clearly in the patterns of Gr-loaded cellulose films. This may be due to the low amount of ordered layer structure of graphene. It is probable that, at low loading, exfoliation and random distribution of the platelets within the cellulose matrices may take place. This may be also due to matrix effect of cellulose which is present at higher content in the films.

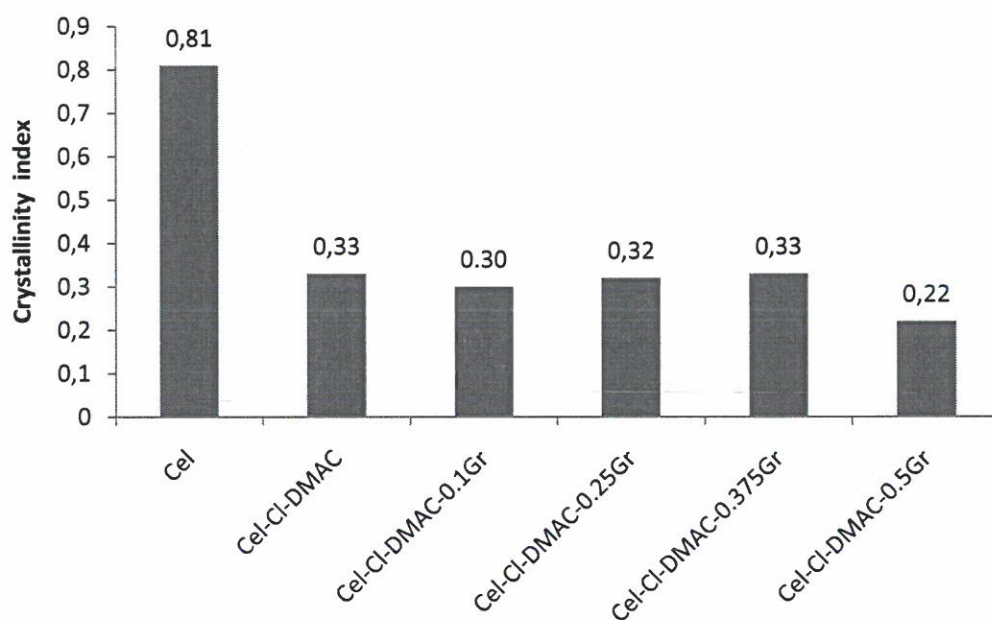


Figure 3.11 Degree of CI of cellulose, Cel-Cl-DMAC and Gr loaded Cel-Cl-DMAC using Segal's equation

The CI of Cellulose was obtained to be around 0.81. When Cel was dissolved in BmimCl and DMAC solution, the CI decreased to 0.33. After loading of graphene

into Cel-Cl-DMAC, the CI of Gr loaded Cel-Cl-DMAC slightly changed(see Figure 3.11). CI values for Cel-Cl-DMAC-0.1Gr, Cel-Cl-DMAC-0.25Gr, Cel-Cl-DMAC-0.375Gr, and Cel-Cl-DMAC-0.5Gr were determined as 0.30, 0.32, 0.33, and 0.22, respectively. It is remarkable that the lowest value of CI was observed for the sample containing the highest graphene content. Graphene of 0.5g decreased significantly the crystallinity of cellulose. Moreover it can be said that loading of graphene at ratios of 0.1%, 0.25% and 0.375% did not lead to considerable variation in terms of crystallinity index.

Table 3.3 The Crystallite size for the samples

Sample Names	Crystallite size(nm)
Cel	6.15
Cel-Cl-DMAC	1.18
Cel-Cl-DMAC-0.1Gr	0.78
Cel-Cl-DMAC-0.25Gr	0.70
Cel-Cl-DMAC-0.375Gr	0.71
Cel-Cl-DMAC-0.5Gr	Not calculated

Table 3.3 shows that the 200 plane apparent crystallite size of Cel, Cel-Cl-DMAC and Gr loaded Cel-Cl-DMAC films was 6.15 ,1.18 , 0.78 ,0.70 and 0.71, respectively. These decrements may be attributed to the fact that the solvent ILs severely damaged the crystal structure of cellulose. Similarly, Liu et al. investigated the crystallite size of Cel which was dissolved in ILs and DMAC and obtained similar result (Liu et al., 2012). Graphene loading to Cel-Cl-DMAC reduced the crystallite size of Cel-Cl-DMAC films.

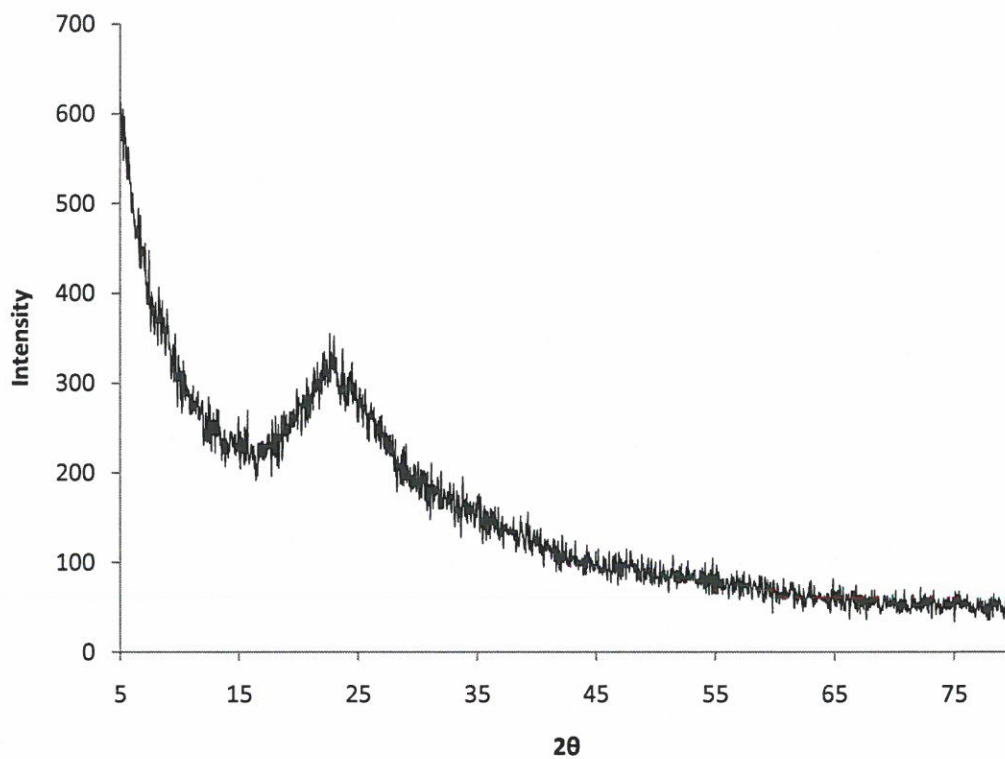


Figure 3.12 X-ray diffraction pattern of Cel-Cl-DMAC

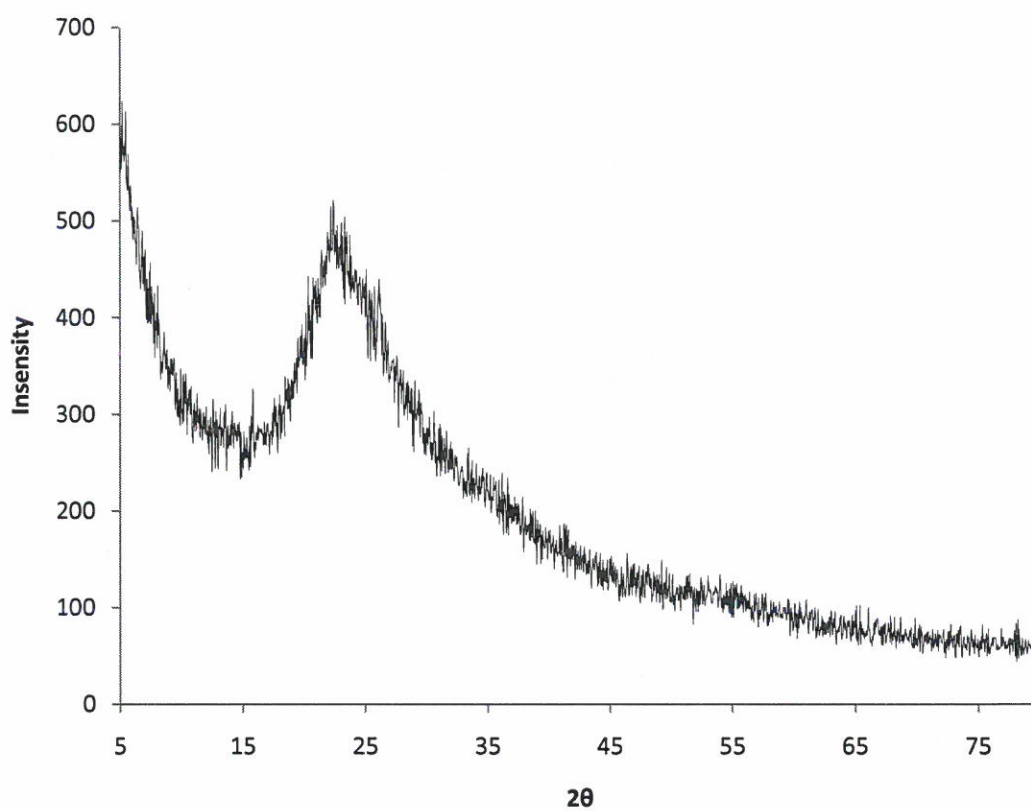


Figure 3.13 X-ray diffraction pattern of Cel-Cl-DMAC -0,1Gr

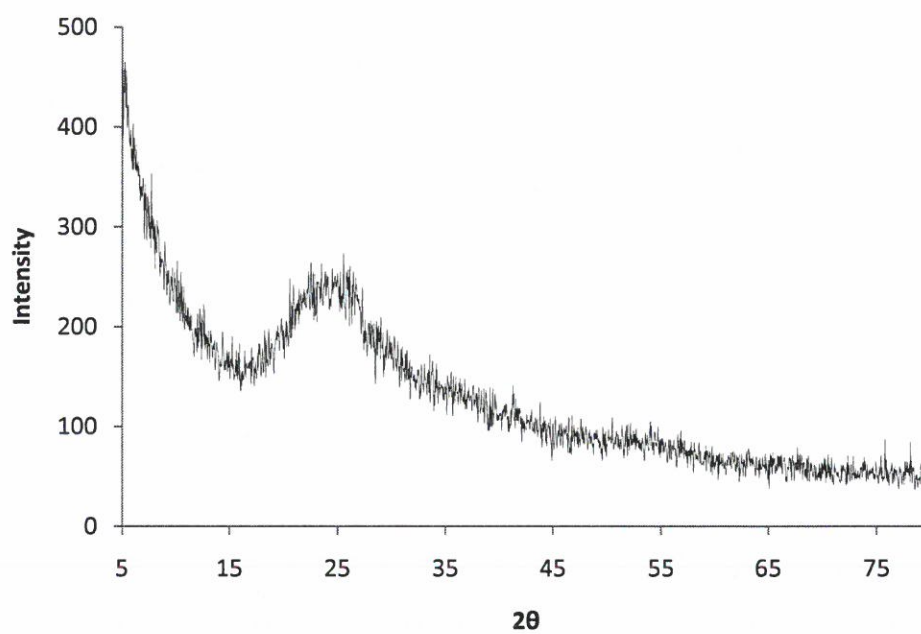


Figure 3.14 X-ray diffraction pattern of Cel-Cl-DMAC -0,25Gr

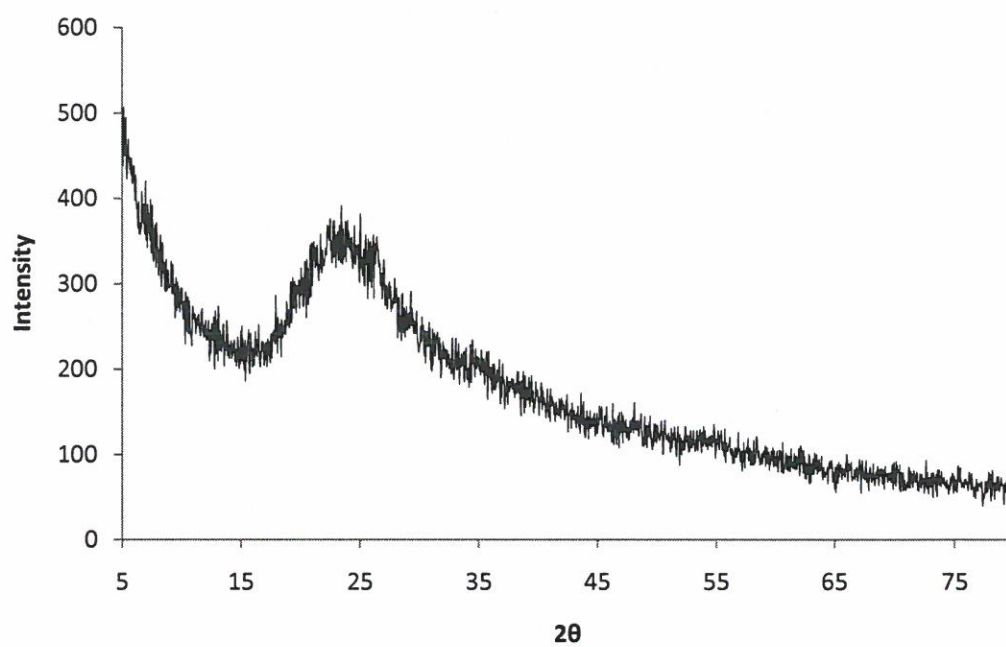


Figure 3.15 X-ray diffraction pattern of Cel-Cl-DMAC -0,375Gr

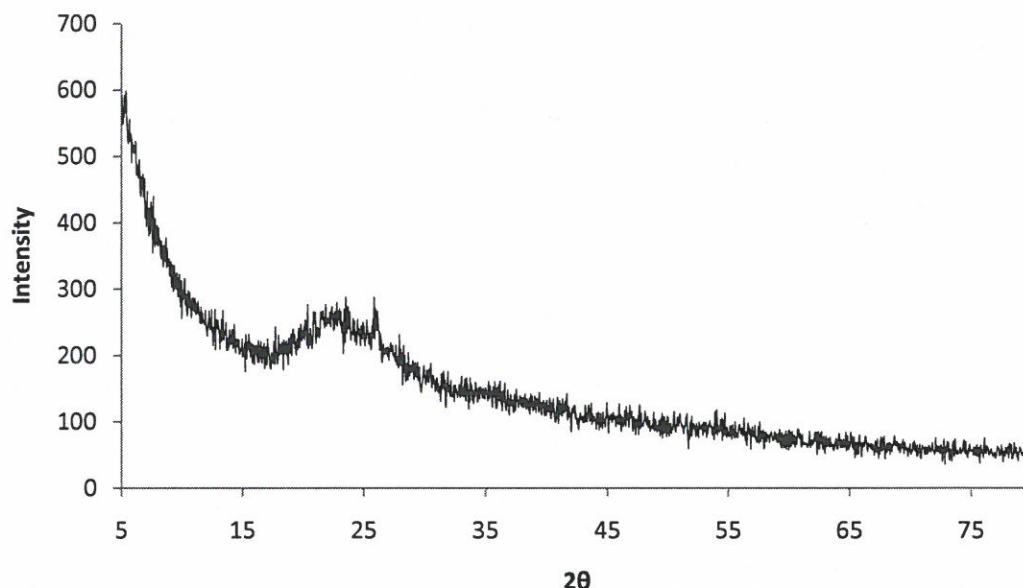


Figure 3.16 X-ray diffraction pattern of Cel-Cl-DMAC -0,5Gr

3.4 Scanning Electron Microscope (SEM)

Morphology of samples was studied using a scanning electron microscope (SEM). Representative SEM images of Cel-Cl-DMAC and Cel-Cl-DMAC-Gr composites are given in Figures 3.17-3.22. As can be seen from Figure 3.17-3.18 cellulose particles were disorderly dispersed in micro-dimension size (see Figure 3.19) as well as in nano-dimension size (see Figures 3.17 and 3.18). Figure 3.18 exhibited nanosize cellulose particles in the range about 50-200 nm. It can be also said that Figure 3.16 exhibited a more compacted morphology in terms of cellulose dispersion. This dispersion of cellulose has been caused by the solvating action of the BmimCl. As shown in Figures 3.19-3.21, after graphene sheets had been dispersed in cellulose film, chain entangling of cellulose increased. Figure 3.21 shows the graphene sheets dispersed in cellulose film, which contains the greatest graphene content this study, can be clearly seen. However for graphene contents of 0.1%, 0.25% and 0.375%, graphene sheets cannot be seen clearly in cellulosic film. This may be due to high level of homogeneity which implies that cellulose and graphene are unified. Previous SEM observation by Han et al.,(2011) reported that the RC/graphene oxide nanocomposites exhibited high level of homogeneity which indicates that cellulose and graphene are unified (Mahmoudian, Wahit, Imran, Ismail & Balakrishnan, 2012).

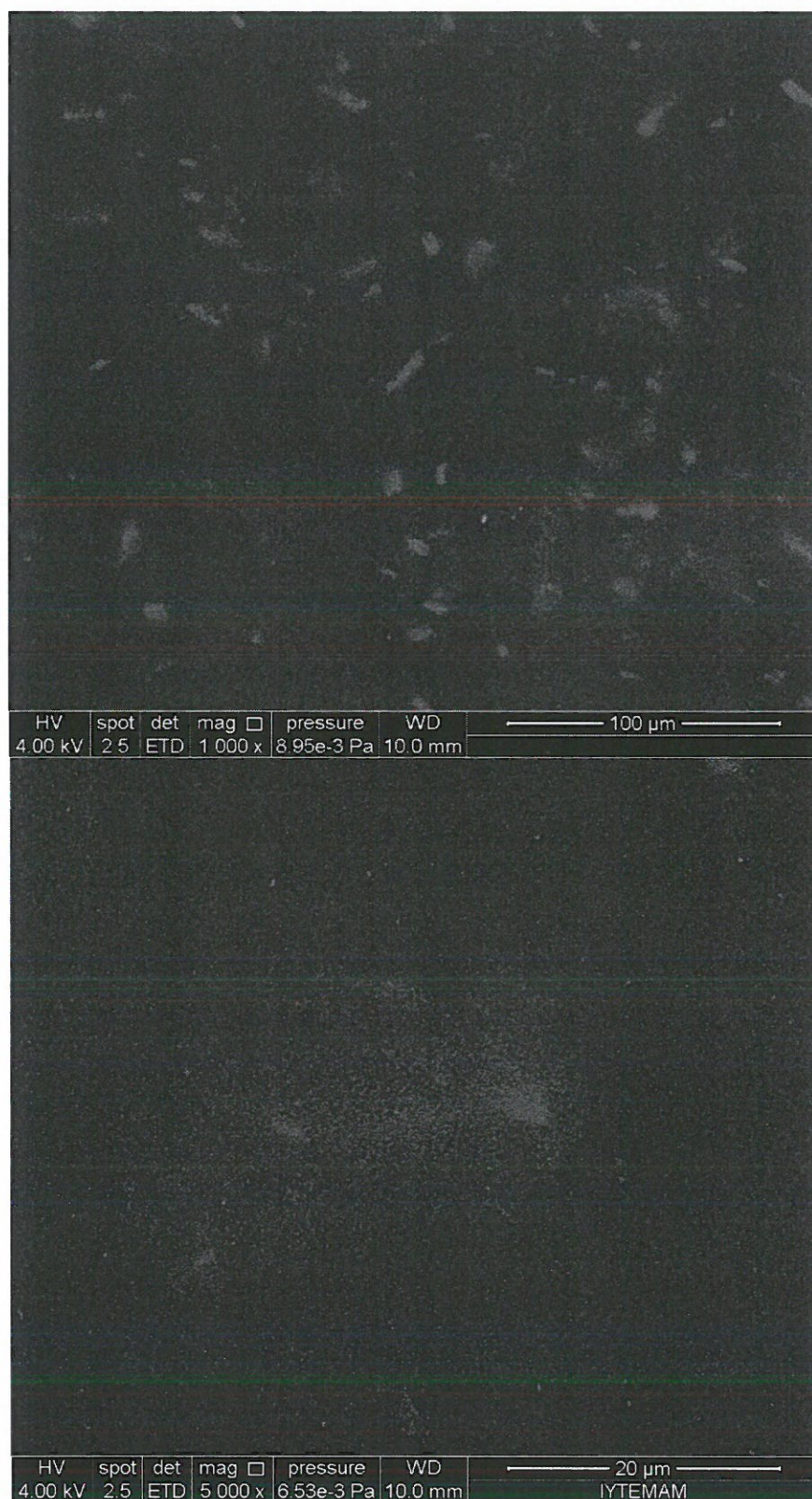


Figure 3.17 SEM images of Cel-Cl-DMAC at magnifications of 1000x and 5000x

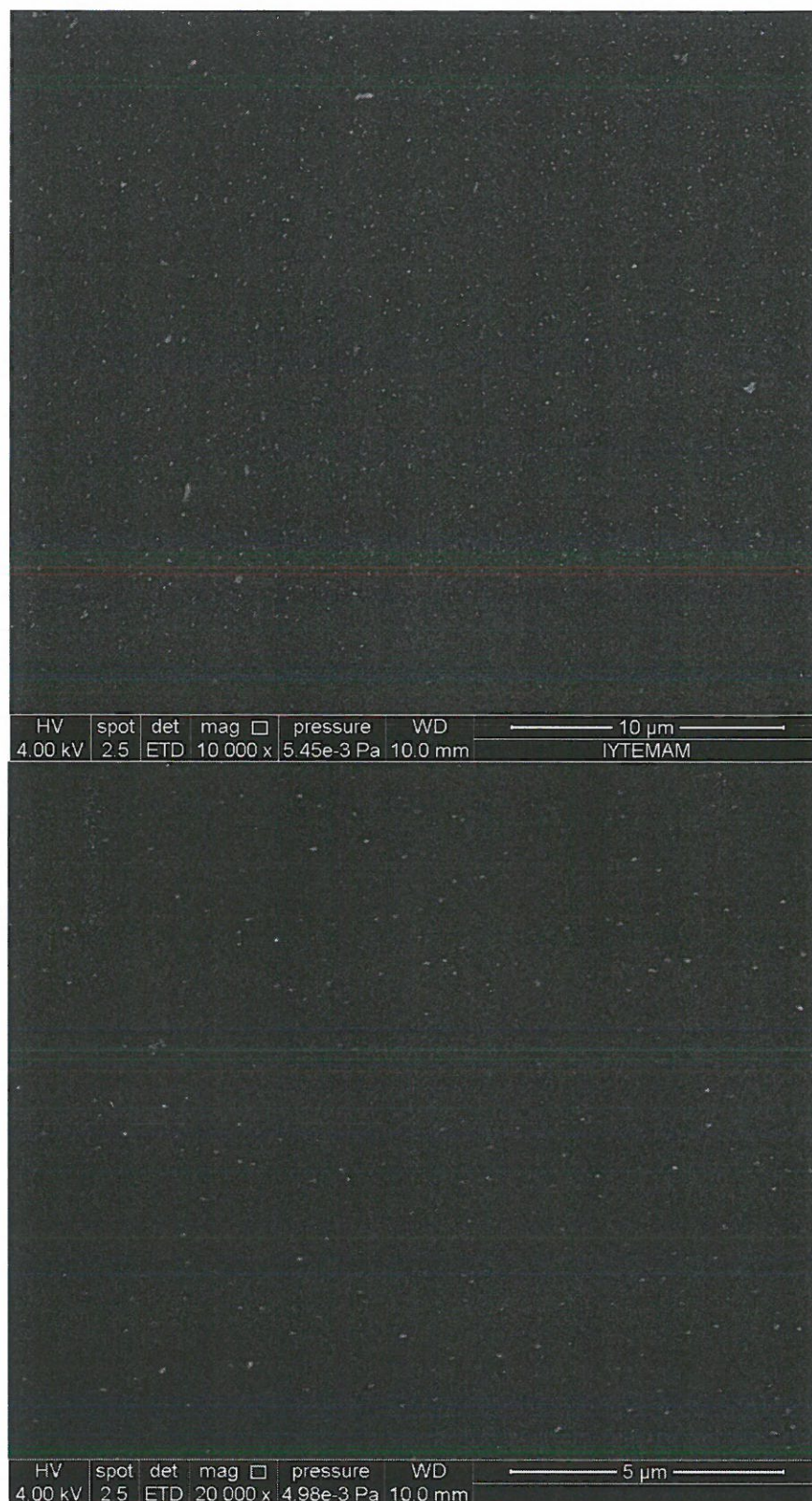


Figure 3.18 SEM images of Cel-Cl-DMAC at magnifications of 10000x and 20000x

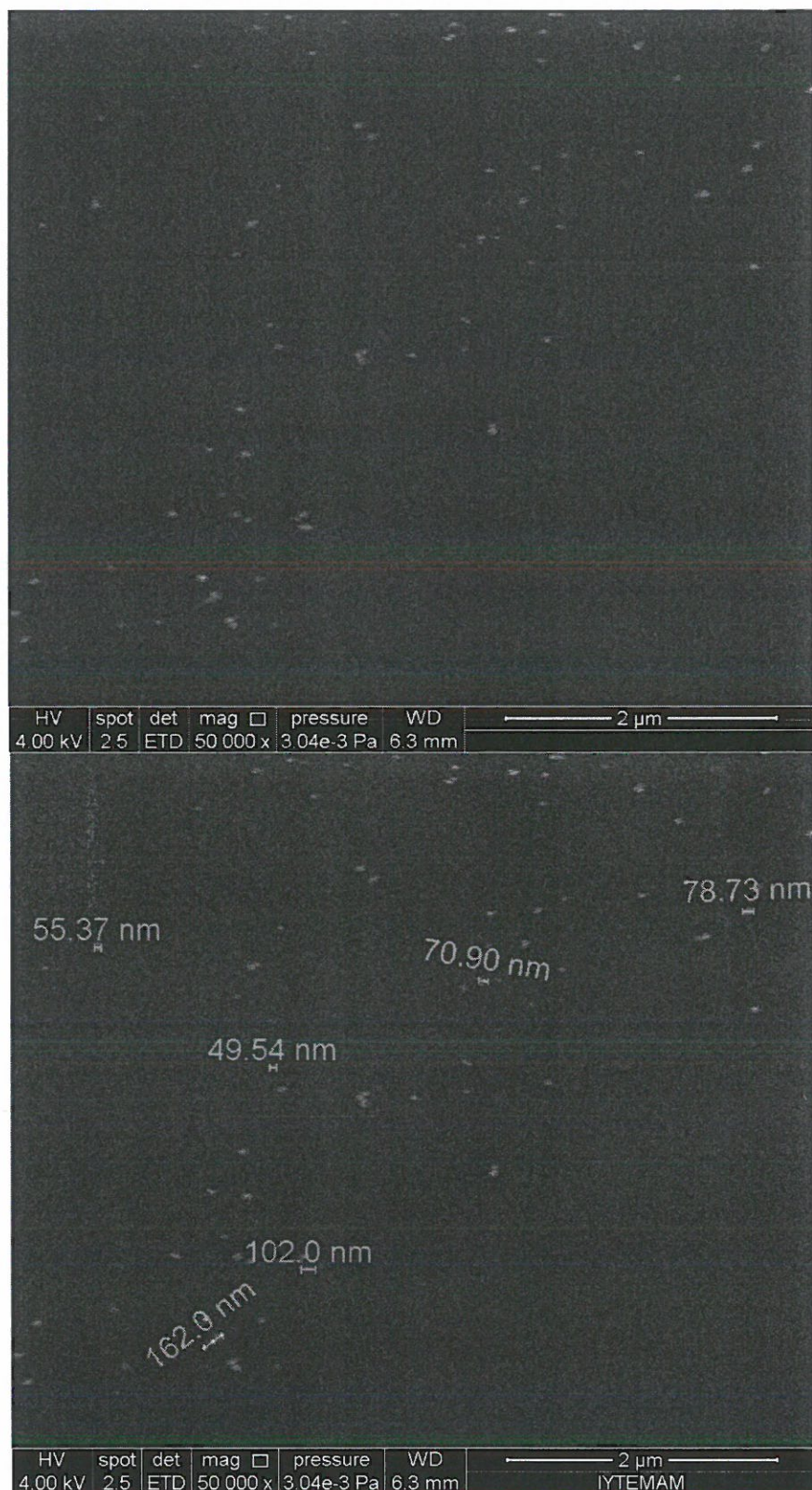


Figure 3.19 SEM images of Cel-Cl-DMAC at magnification of 50000x

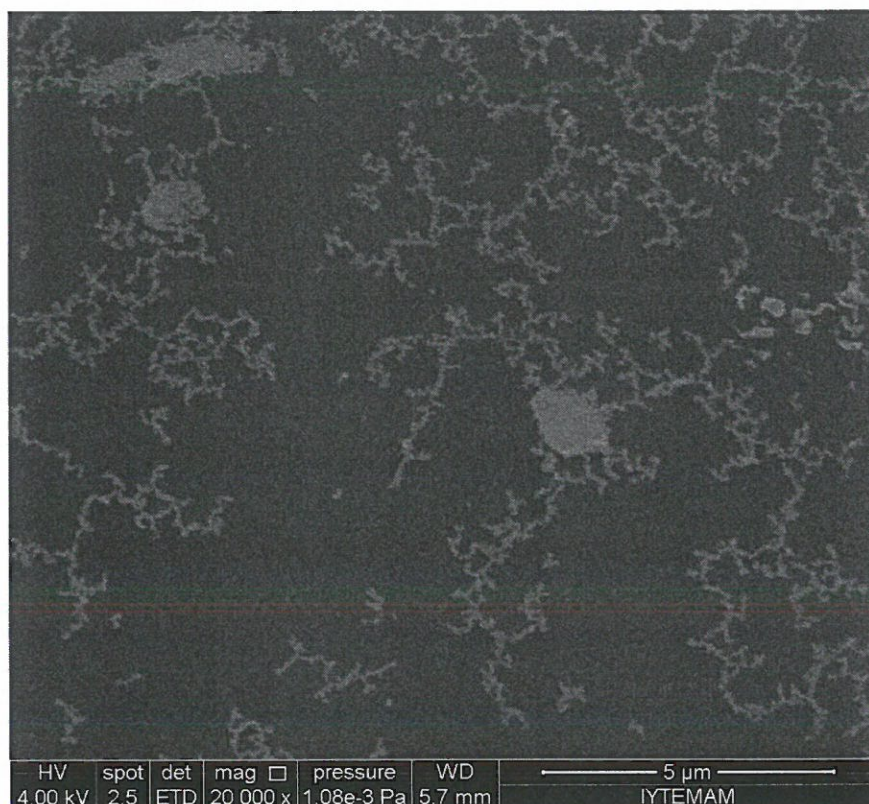


Figure3.20 SEM images of Cel-Cl-DMAC-0.1Gr at magnification of 20000x

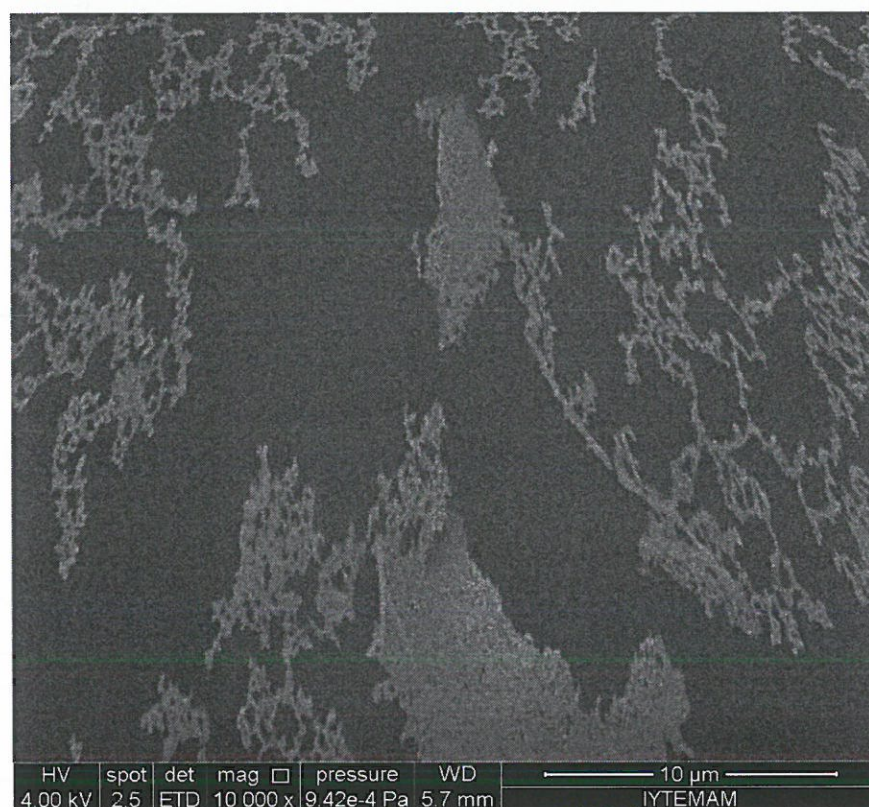


Figure 3.21 SEM images of Cel-Cl-DMAC-0.25Gr at magnification of 10000x

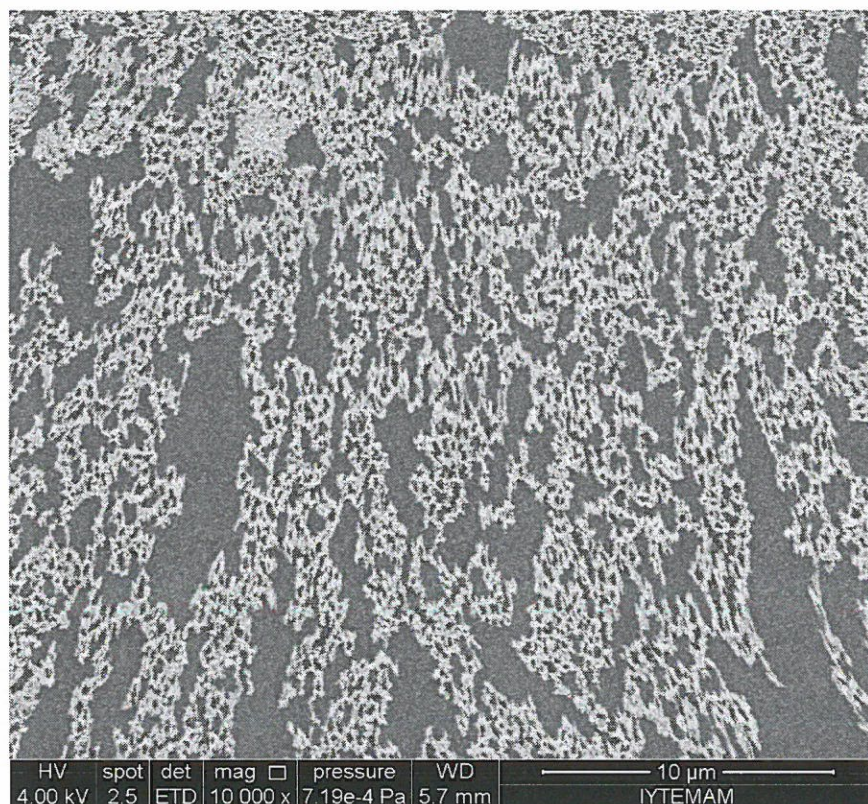


Figure 3.22 SEM images of Cel-Cl-DMAC-0.375Gr at magnification of 10000x

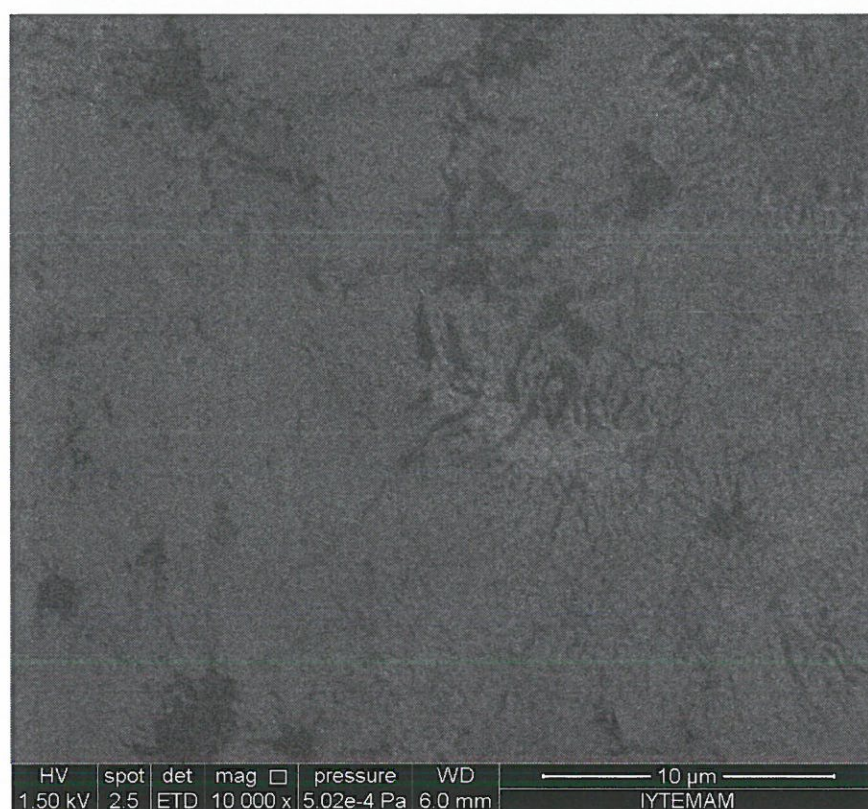


Figure 3.23 SEM images of Cel-Cl-DMAC-0.5Gr at magnification of 10000x

3.5 Mechanical Properties

The effects of graphene loading on tensile strength and Young's modulus on Cel-Cl-DMAC based films and Cel-Cl-DMAC actuator films are shown in Figures 3.24 and 3.25, respectively. The results are also summarized in Table 3.4. Tensile strength and Young's modulus of Cel-Cl-DMAC films were obtained to be 15.63 MPa and 0.62 GPa, respectively. After gold coating on surface of Cel-Cl-DMAC tensile strength and Young's modulus increased by 28.4% and 14.5%, respectively. After 0.1% of Graphene was loaded into Cel-Cl-DMAC, tensile strength and tensile modulus of Cel-Cl-DMAC film increased to 18.67 MPa and 0.73 GPa and so resulting in 19.4% and 17.7%, respectively. After gold coating on surface of Cel-Cl-DMAC-0.1Gr films tensile strength and tensile modulus increased to 23.67 MPa and 0.87 GPa, respectively. This treatment led to 28.4% and 19.4% increases over untreated Cel-Cl-DMAC actuator film. When 0.25% of graphene was used for modification of Cel-Cl-DMAC, better results in terms of tensile properties were observed. Namely, tensile strength and Young modulus increased to 22.25 MPa and 0.81 GPa, which indicates 44.91% and 30.65% increases, respectively, for Cel-Cl-DMAC-0.25Gr films when compared to Cel-Cl-DMAC film. In addition to these, after gold had been coated on the surface of Cel-Cl-DMAC-0.25Gr films tensile strength and Young's modulus values were obtained to be 26.14 MPa and 0.93 GPa, respectively. In comparison with tensile strength and Young's modulus of Cel-Cl-DMAC actuator film, 45.61 % and 22.54 % increases were observed for Cel-Cl-DMAC-0.25Gr actuator films. After 0.375% of graphene was used for modification of Cel-Cl-DMAC film, tensile properties were improved significantly. Tensile strength and Young's modulus values were determined to be 26.14 MPa and 0.89 GPa, respectively. In other words, tensile strength and tensile modulus of Cel-Cl-DMAC actuator increased by 67.24% and 43.55%, respectively. Moreover, tensile strength and Young's modulus of Cel-Cl-DMAC-0.375Gr actuator film were obtained as 34.46 MPa and 0.93 GPa, resulting in 71.96% and 31% higher than those of Cel-Cl-DMAC actuator film. Tensile strength and tensile modulus of Cel-Cl-DMAC film and Cel-Cl-DMAC actuator film increased up to graphene concentration of 0.375% beyond which tensile properties started to decrease. These increments may be explained by well dispersion of graphene into the mixture of Cellulose,

BmimCl, and DMAC. But at relatively high load (0.5%), it is likely that graphene was not well-dispersed in the above-stated mixture. When the concentration of graphene increased to 0.5%, tensile strength and tensile modulus of Cel-Cl-DMAC films and Cel-Cl-DMAC actuators decreased considerably. For example tensile strength and Young's modulus of Cel-Cl-DMAC-0.5Gr actuator film were found to be 26.67 MPa and 0.78 GPa, respectively. When compared to those values of Cel-Cl-DMAC actuator film, an increment of 33.08 % in tensile strength and a decrement of 9.86% in Young's modulus were noticed. Tensile strength and tensile modulus for Cel-Cl-DMAC-0.5Gr film were calculated to be 20.06 MPa and 0.71 GPa, respectively. When compared to those values of Cel-Cl-DMAC film, increments of 28.34% in tensile strength and 16.39% in Young's modulus were observed.

Previously, a few papers have also reported something on the preparation and mechanical properties of Graphene reinforced polymers (such as nafion, natural polymer and polybenzimidazole etc). For example, Y.Wang has demonstrated a 24% increase in modulus of polybenzimidazole (Wang, Shi, Fang, Xu & Yin, 2011) by the incorporation of 1% Graphene oxide into polybenzimidazoles. T.Kulia et.al have prepared functionalized graphene/linear low density polyethylene (LLDPE) composites by a solution mixing method using dodecyl amine. The tensile strength of the composite increased with 3 wt.% of dodecyl amine-graphene loading and was 46% higher than that of neat LLDPE (Kula et al., 2011). Jung et al., fabricated electro-active actuators based on graphene reinforced nafion composite electrolytes and they obtained mechanical properties of graphene reinforced nafion composite. The tensile strength of-nafion ionic membrane was significantly increased up to 200% by loading 1.0 wt.% graphene, and Young's modulus was more than two times with a minute loading of graphene to Nafion electrolyte(Jung, Jeon, Sridhar & Oh, 2011).

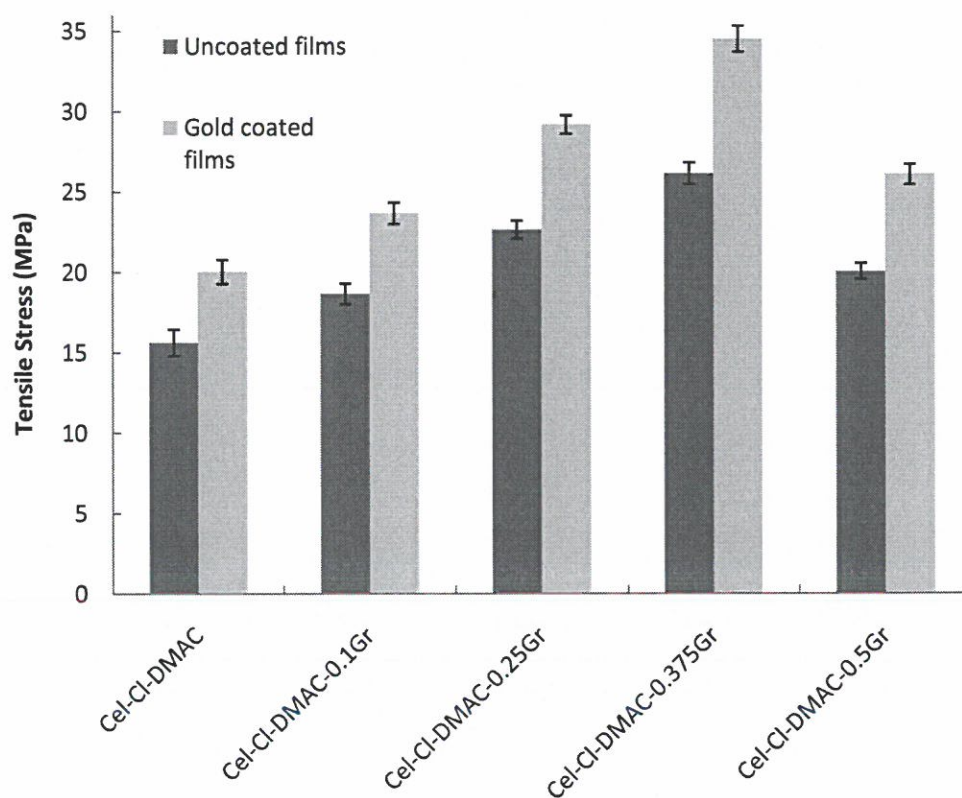


Figure 3.24 Effect of Gr loading on tensile strength of gold coated Cel-Cl-DMAC

Table 3.4 Mechanical properties of Cel-Cl-DMAC and Gr loaded Cel-Cl-DMAC

Specimen Name	Tensile Stress (MPa)		Elasticity modulus (GPa)	
	Uncoated films	Gold coated films	Uncoated films	Gold coated films
Cel-Cl-DMAC	15.63±0.82	20.04±0.75	0.62±0.03	0.71±0.04
Cel-Cl-DMAC-0.1Gr	18.67±0.64	23.67±0.67	0.73±0.04	0.78±0.04
Cel-Cl-DMAC-0.25Gr	22.65±0.57	29.18±0.57	0.81±0.05	0.87±0.02
Cel-Cl-DMAC-0.375Gr	26.14±0.68	34.49±0.81	0.89±0.04	0.93±0.06
Cel-Cl-DMAC-0.5Gr	20.06±0.49	26.07±0.62	0.71±0.05	0.78±0.02

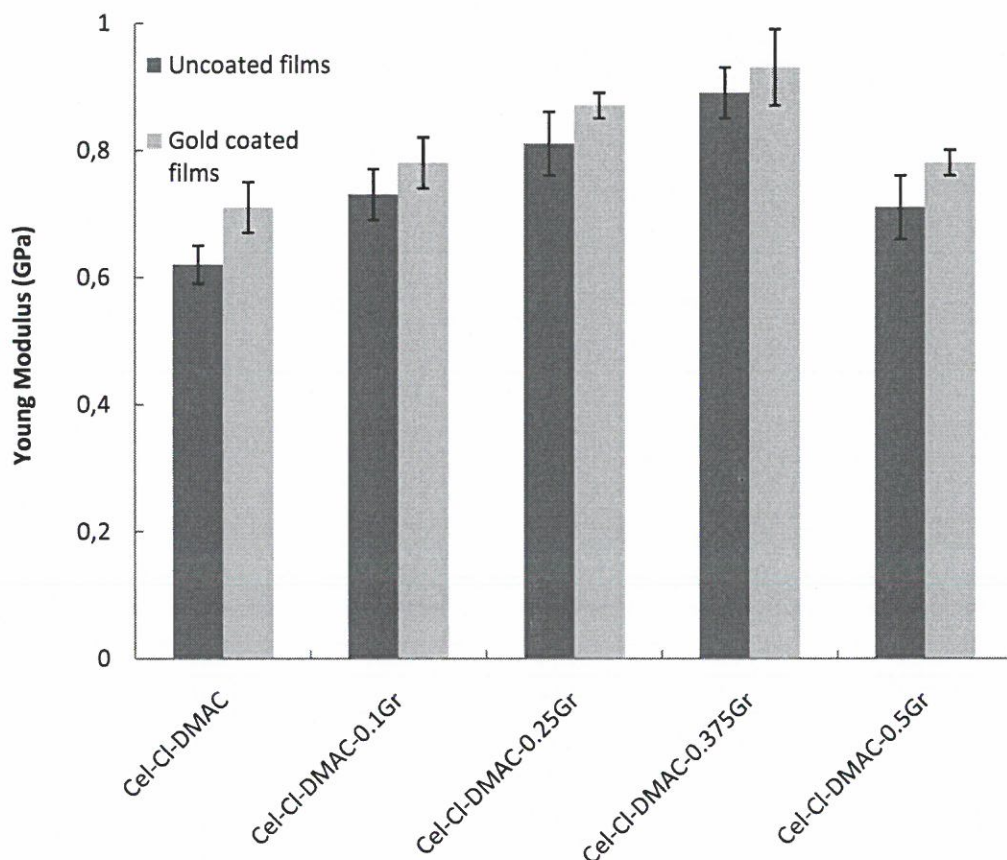


Figure 3.25 Effect of Gr loading on Young's modulus of gold coated Cel-Cl-DMAC

3.6 Electrical Properties

Figure 3.26 shows the relationship between the change in electrical conductivity and the graphene content. Electrical conductivity value for Cel-Cl-DMAC was obtained to be $3.5 \times 10^{-3} \text{ S cm}^{-1}$. After 0.1% Gr was loaded into the mixture of Cel-Cl-DMAC, the film shows a electrical conductivity value of $4 \times 10^{-3} \text{ S cm}^{-1}$. This increment reflects 14% higher conductivity. Increasing of graphene content to 0.25% in the above-stated mixture led to an increase in electrical conductivity from $3.5 \times 10^{-3} \text{ S/cm}$ to $4.6 \times 10^{-3} \text{ S/cm}$. Namely graphene of 0.25% caused 31% increase in electrical conductivity. After Graphene of 0.375% was used for modification of Cel-Cl-DMAC

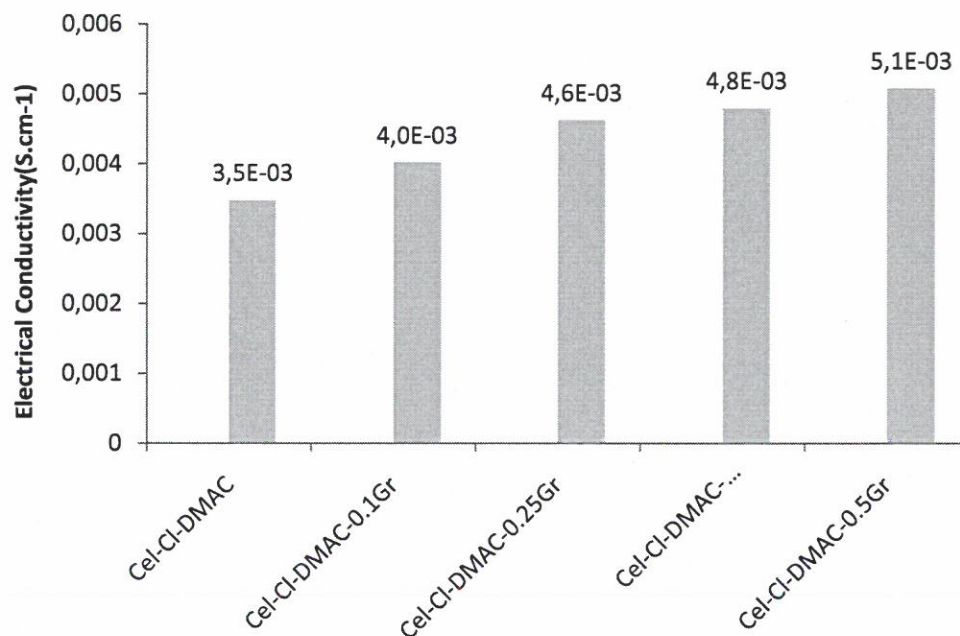


Figure 3.26 Electrical Conductivity of Cel-Cl-DMAC and loaded Cel-Cl-DMAC films

film, electrical conductivity was measured to be 4.8×10^{-3} S/cm, which indicates 37% increase. Loading of Cel-Cl-DMAC film with the highest graphene concentration in this study, 0.5%, caused the greatest electrical conductivity in this study, that is, 5.1×10^{-3} S/cm. When compared the electrical conductivity value of Cel-Cl-DMAC, an increment of 46% was determined. As can be seen in Figure 3.18, the electrical conductivity of Cel-Cl-DMAC increased from 3.5×10^{-3} to 5.1×10^{-3} S/cm while the graphene content was increased from 0% to 0.5%. An important reason for improvement in proton conductivity values may be attributed to combinations of highly conductive graphene in the Cel-Cl-DMAC (Hazarika & Jana, 2013). Jung et al. investigated the proton conductivity of electro-active actuators based on graphene reinforced Nafion composite electrolytes. Graphene loading to nafion improved the proton conductivity of nafion actuator, as was expected (Jung, Jeon, Sridhar & Oh, 2011)

3.7 Electroactive Properties

For DC responses, the time histories of the tip displacements for recast Cel-Cl-DMAC and Gr loaded Cel-Cl-DMAC actuators under a DC signal of a maximum voltage of $3V_{DC}$, $5V_{DC}$ and $7V_{DC}$ are shown in Figure 3.27-3.56. Besides, Table 3.5

shows the maximum tip displacements of Cel-Cl-DMAC and Gr loaded Cel-Cl-DMAC actuators. However, generally, IPMC actuators are evaluated with tip displacement-time graphs. Time evolutions of the tip displacement (time response) of the actuators are shown in Figure 3.41-3.56.

These experiments exhibited a different response form for some actuator samples. For example, for Cel-Cl-DMAC-0.1Gr actuators, while the maximum tip displacement under $3V_{DC}$ is 1.5 mm, the maximum tip displacement under an application of $-3V_{DC}$ is 0.8 mm. As shown in Table 3.5, for $3V_{DC}$ the Cel-Cl-DMAC-0.25Gr actuator showed greater tip displacement than another actuators. But, when voltage was increased to 7V, tip displacement reduced abruptly. Similarly, for Cel-Cl-DMAC-0.5Gr actuators, when voltage was raised, tip displacements decreased.

In the study of J.Jung et.al, electro-active actuators based on graphene reinforced Nafion composite electrolytes were produced and their actuation performances were examined. They obtained that graphene loading greatly improves the harmonic responses, the blocking force and the energy efficiency in Nafion-based ionic polymer-metal composite actuators (Jung, Jeon, Sridhar & Oh, 2011). The tip displacement of the 1.0 wt.% graphene-reinforced actuator is almost two times that of the recast Nafion-based ionic polymer-metal composite (IPMC) actuator. The similar improvement was observed in our study as well. Another study ,CNT was added in Nafion developed by J.Yip et al. whose experiment was carried out by applying $4.5V_{DC}$ (Yip et al., 2012). This experiment's results showed that the maximum tip displacements of Cel-Cl-DMAC and Gr loaded Cel-Cl-DMAC actuators were higher than that of graphene added Nafion actuators.

The improvement of tip displacement by graphene treatment may be due to the enhanced proton conductivity of polymer, electron transport behavior of graphene and ionic exchangeable capacity(Jung, Jeon, Sridhar & Oh, 2011). Platelet structure of graphene may be another reason for this improvement. In a typical actuator, it is known that under electrical field, fast bending motion toward one of the electrodes takes place and then a slow relaxation towards the other electrode is seen. This case is due to the migration of hydrated cations and diffusion of water from these cluster regions through the nano-channels (Paquette & Kim, 2004). Therefore graphene

may block or delay the water migration. The platelet morphology of graphene will delay this water migration due to its “tortuous path”. It was noted that low content of graphene may be favourable vis-à-vis other carbonaceous nano-fillers such as SWNCTs or MWNCTs. And it can be stated that c based actuators (Jung, Jeon, Sridhar & Oh, 2011).

When actuator response is analyzed with reference to time scale, the greater voltage values lead to the faster transportation process in molecular level and this result in smaller increment in tip displacement. Therefore, the tip displacement against time curves can be approximated to be in exponential form:

$$x_{dc}(t) = X_{\max} (1 - e^{-\frac{t}{T}}) \quad (3.1)$$

where $X_{\max}$ is the maximum tip displacement and T is time constant. Following this assumption, the time constant and maximum tip displacement values are defined as characteristic parameters of time response of the actuators

The time constants were calculated using the experimental data for Cel-Cl-DMAC and Gr loaded Cel-Cl-DMAC actuators when the input voltage is 3, 5 and 7V. The results are presented in Table 3.6. According to this table, Cel-Cl-DMAC-0.5Gr actuators, as applied voltages increased, time constants of actuators and the maximum displacement decreased. However for Cel-Cl-DMAC-0.25Gr actuator similar result was observed except for the input voltages of 7V and -7V. Time constants for Cel-Cl-DMAC and Cel-Cl-DMAC-0.1Gr actuators could be calculated for the input voltages of 3V and -3V. It is interesting to note that Cel-Cl-DMAC-0.375Gr did not demonstrate actuation performance, neither maximum displacement nor time constant.

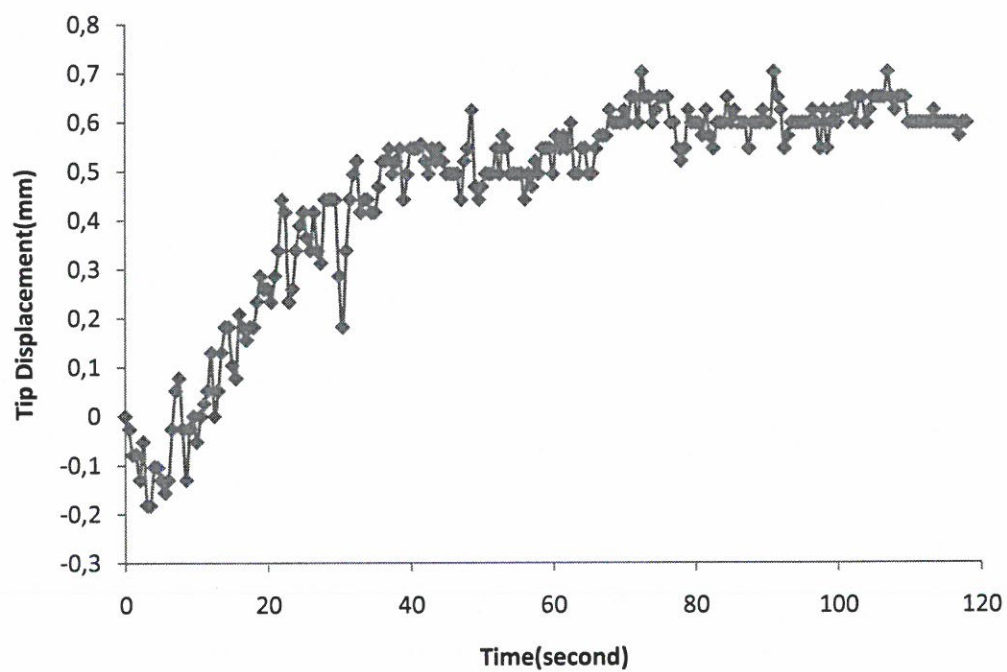


Figure 3.27 The time evolution of the tip displacement (time response) of Cel-Cl-DMAC(3v)

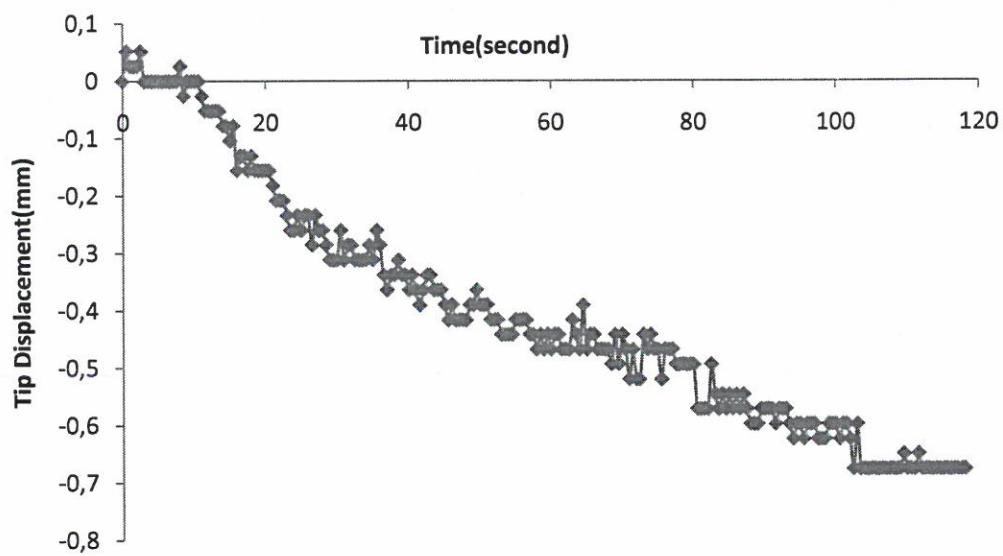


Figure 3.28 The time evolution of the tip displacement (time response) of Cel-Cl-DMAC(-3v)

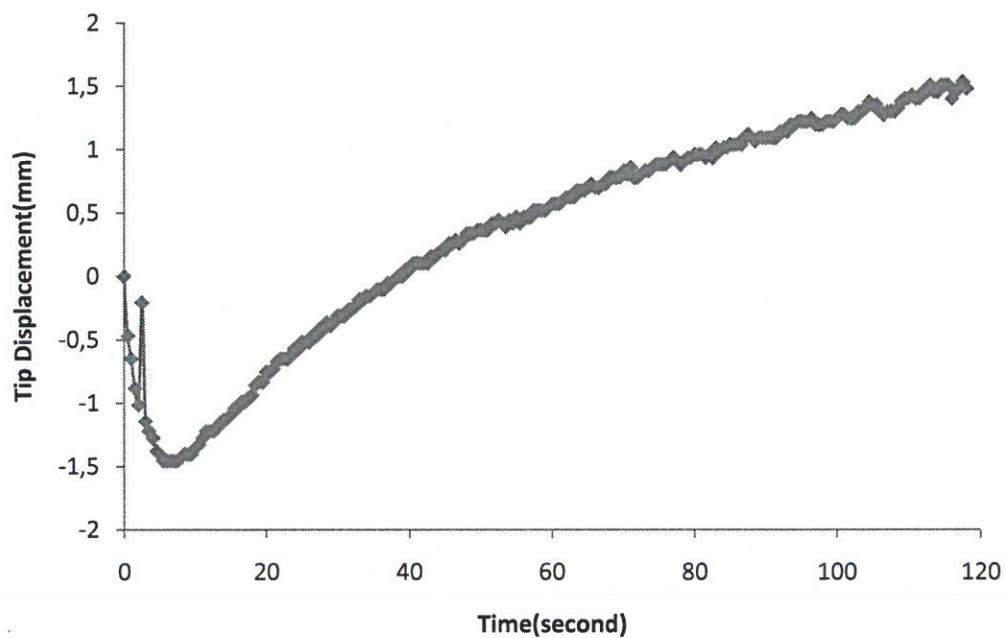


Figure 3.29 The time evolution of the tip displacement (time response) of Cel-Cl-DMAC-0.1Gr(3v)

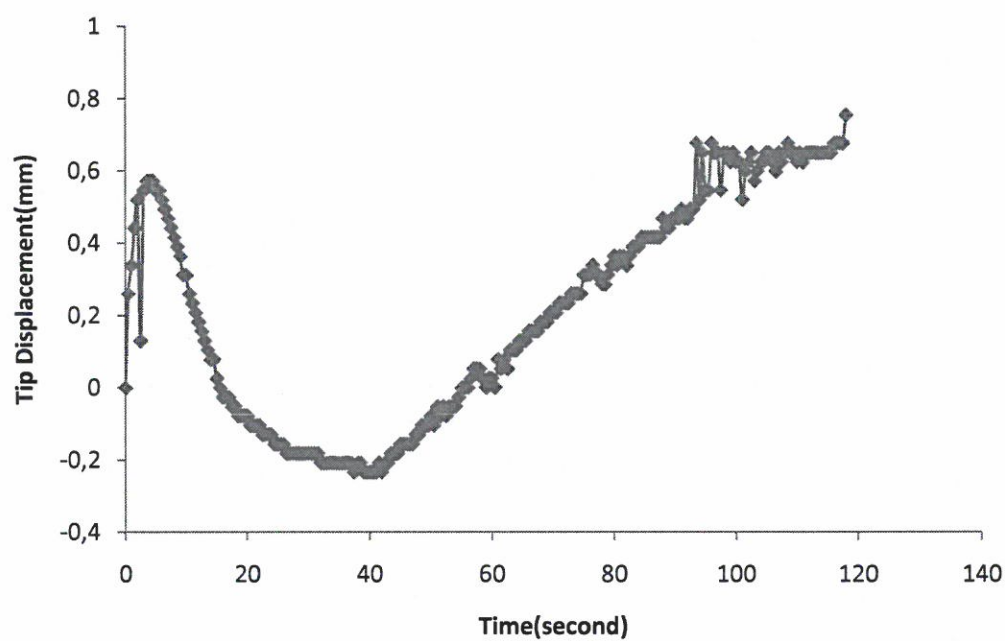


Figure 3.30 The time evolution of the tip displacement (time response) of Cel-Cl-DMAC-0.1Gr(-3v)

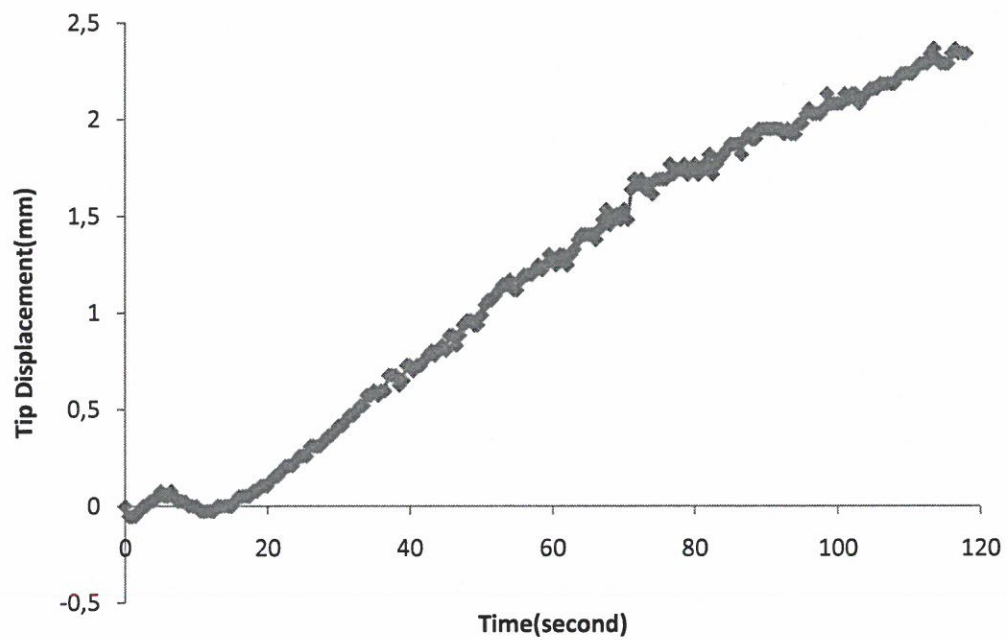


Figure 3.31 The time evolution of the tip displacement (time response) of Cel-Cl-DMAC-0.25Gr(3v)

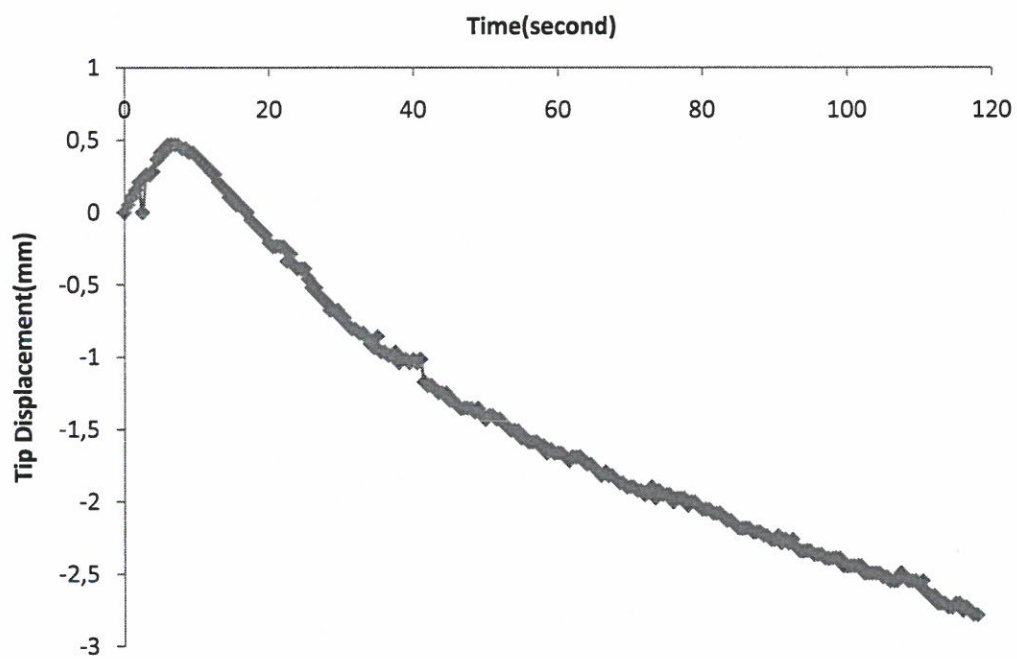


Figure 3.32 The time evolution of the tip displacement (time response) of Cel-Cl-DMAC-0.25Gr(-3v)

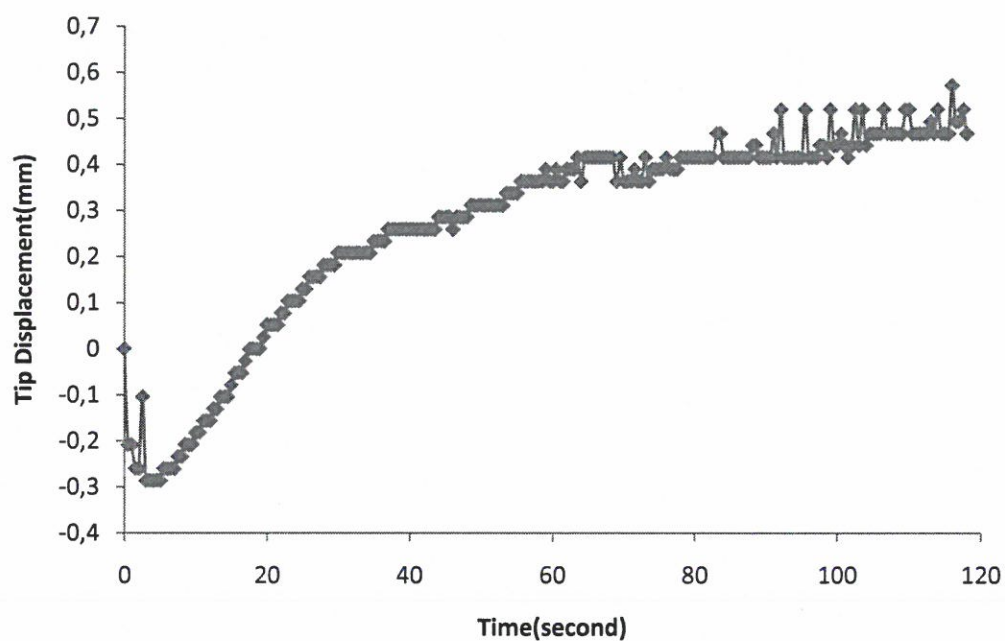


Figure 3.33 The time evolution of the tip displacement (time response) of Cel-Cl-DMAC-0.25Gr(5v)

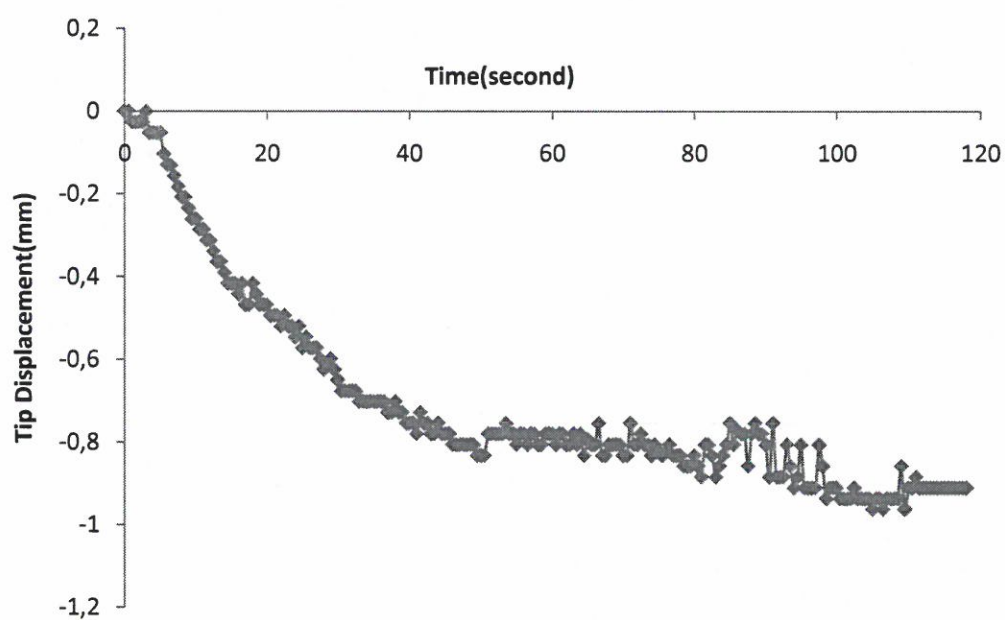


Figure 3.34 The time evolution of the tip displacement (time response) of Cel-Cl-DMAC-0.25Gr(-5v)

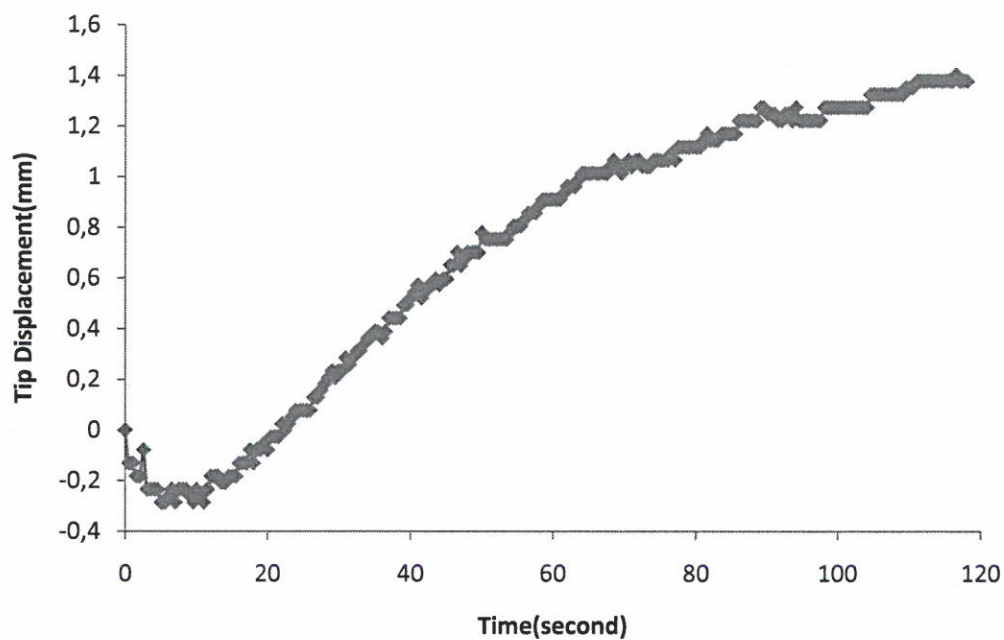


Figure 3.35 The time evolution (second) of the tip displacement (time response) of Cel-Cl-DMAC-0.5Gr(3v)

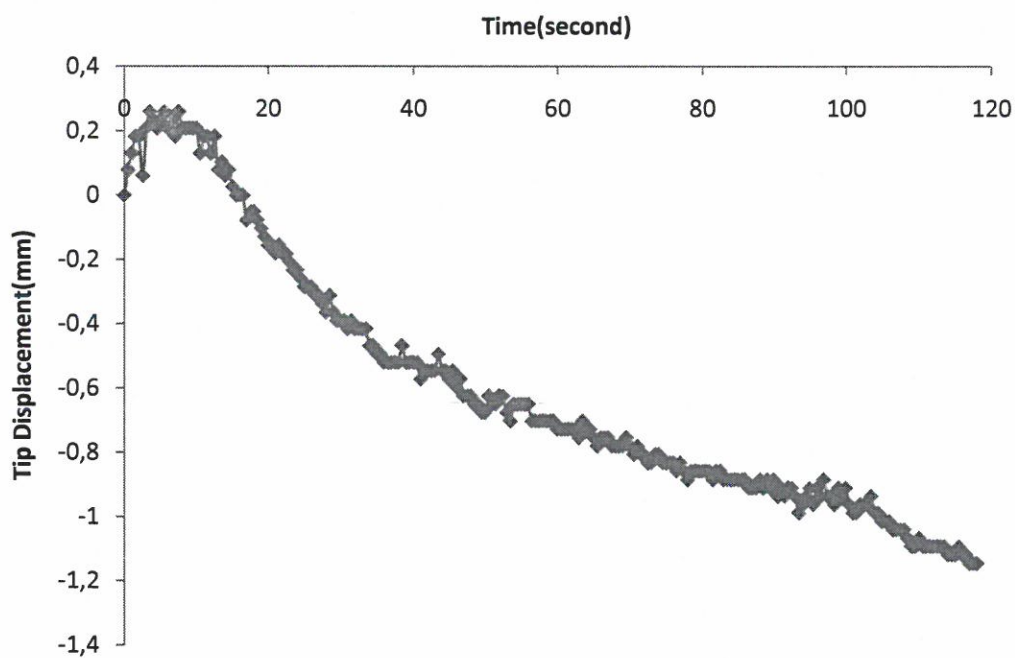


Figure 3.36 The time evolution of the tip displacement (time response) of Cel-Cl-DMAC-0.5Gr(-3v)

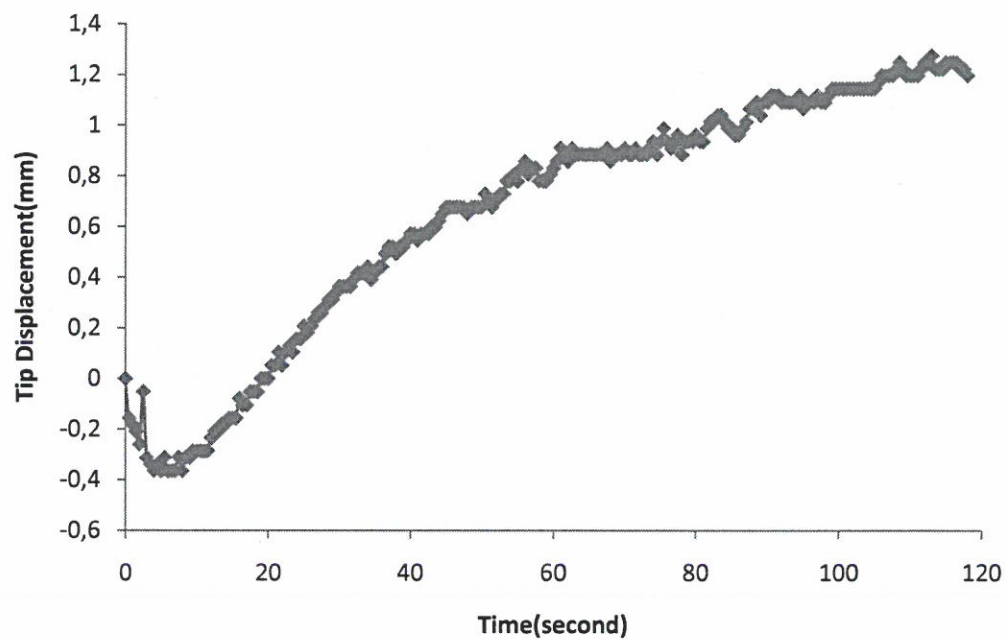


Figure 3.37 The time evolution of the tip displacement (time response) of Cel-Cl-DMAC-0.5Gr(5v)

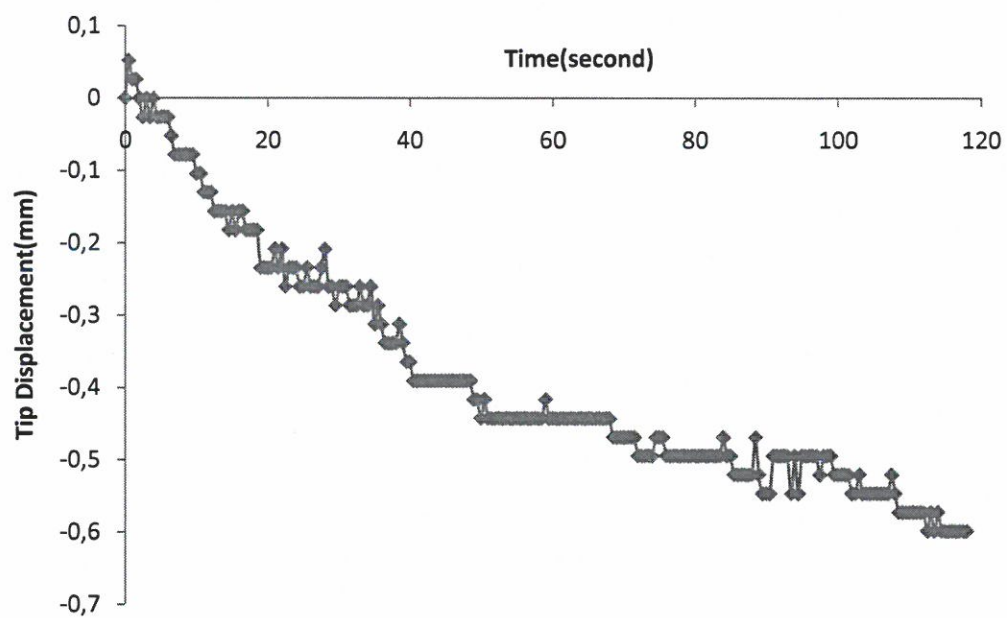


Figure 3.38 The time evolution of the tip displacement (time response) of Cel-Cl-DMAC-0.5Gr(-5v)

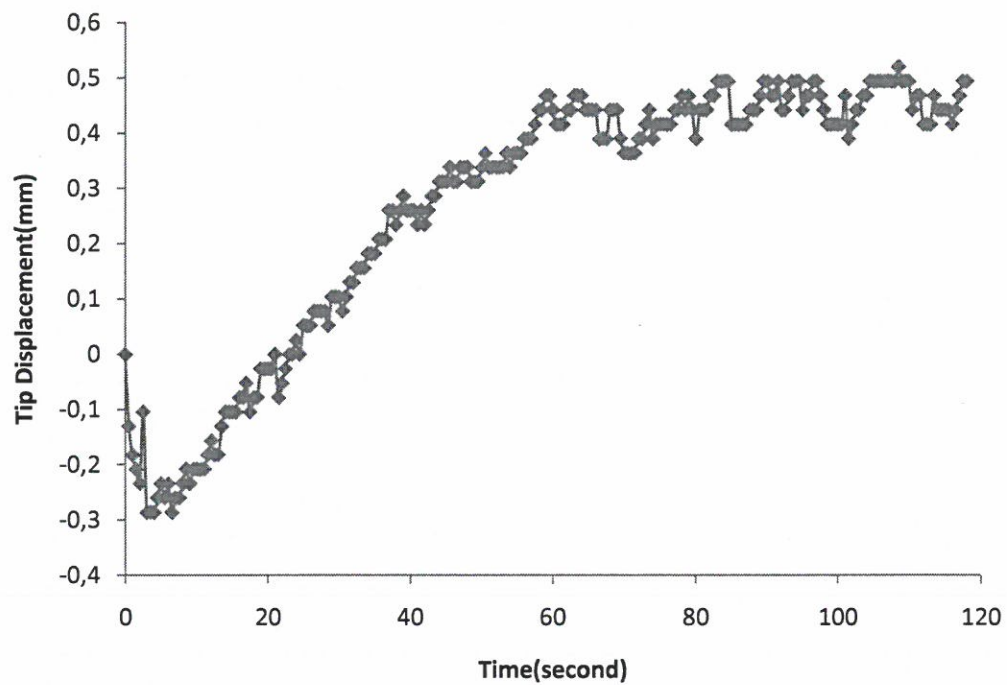


Figure 3.39 The time evolution of the tip displacement (time response) of Cel-Cl-DMAC-0.5Gr(7v)

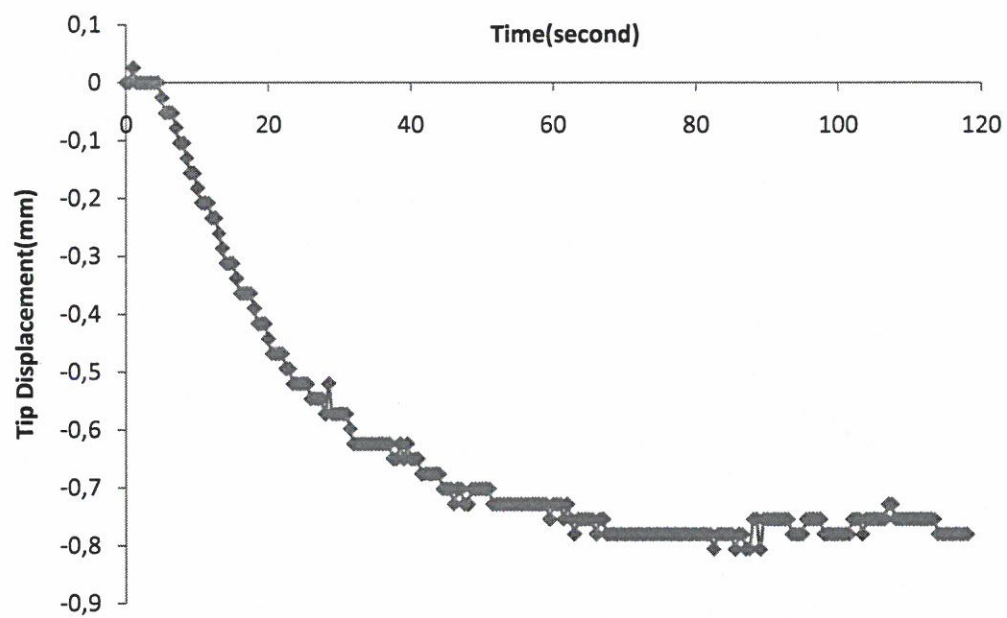


Figure 3.40 The time evolution of the tip displacement (time response) of Cel-Cl-DMAC-0.5Gr(-7v)

Table 3.5 The maximum tip displacements (mm) of Cel-Cl-DMAC and Gr loaded Cel-Cl-DMAC actuators when excited with 3, 5 and 7 volts

Sample Names	3v	-3v	5v	-5v	7v	-7v
Cel-Cl-DMAC	0.6	-0.6	0*	0*	0*	0*
Cel-Cl-DMAC-0.1Gr	1.5	0.8	0*	0*	0*	0*
Cel-Cl-DMAC-0.25Gr	2.2	-2.9	0.5	-0.8	0*	0*
Cel-Cl-DMAC-0.375Gr	0*	0*	0*	0*	0*	0*
Cel-Cl-DMAC-0.5Gr	1.4	-1.4	1.2	-0.65	0.5	-0.7

(*Time evolution of the tip displacement (time response) of the actuators are shown in Figure 3.41-3.56)

Table 3.6 Time constants of Cel-Cl-DMAC and Gr loaded Cel-Cl-DMAC actuators when excited with 3, 5 and 7 volts

Sample Names	3v	-3v	5v	-5v	7v	-7v
Cel-Cl-DMAC	18.5	53	0	0	0	0
Cel-Cl-DMAC-0.1Gr	44	43	0	0	0	0
Cel-Cl-DMAC-0.25Gr	53.5	48.5	25	27.5	0	0
Cel-Cl-DMAC-0.375Gr	0	0	0	0	0	0
Cel-Cl-DMAC-0.5Gr	45	47	36	40.25	33	23.25

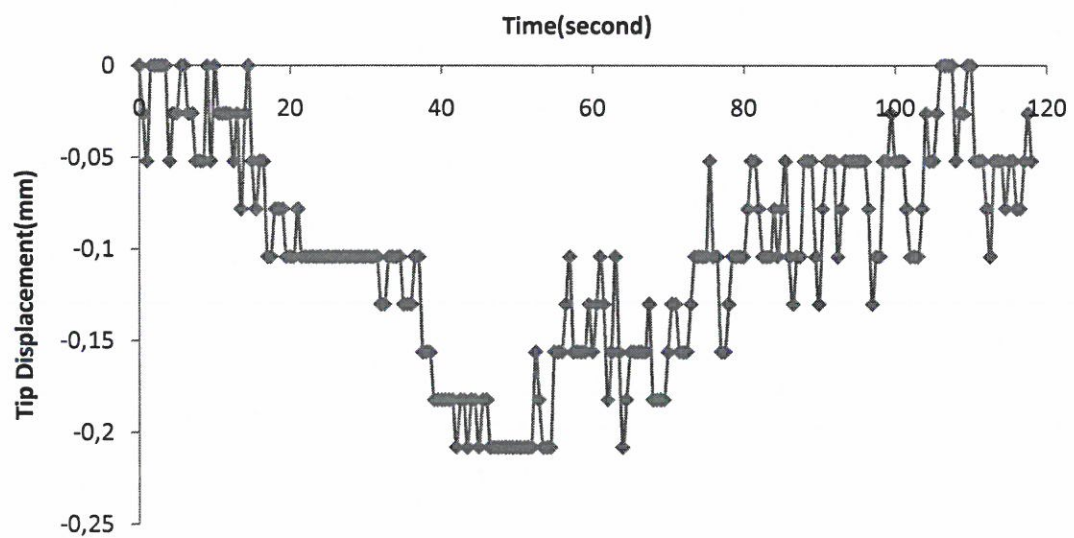


Figure 3.41 The time evolution of the tip displacement (time response) of Cel-Cl-DMAC(5v)

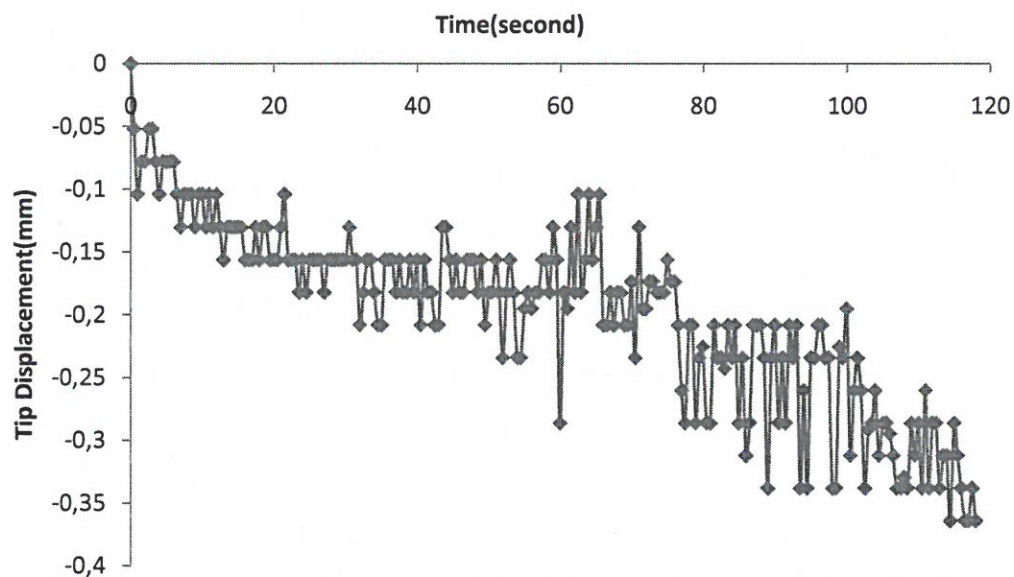


Figure 3.42 The time evolution of the tip displacement (time response) of Cel-Cl-DMAC(-5v)

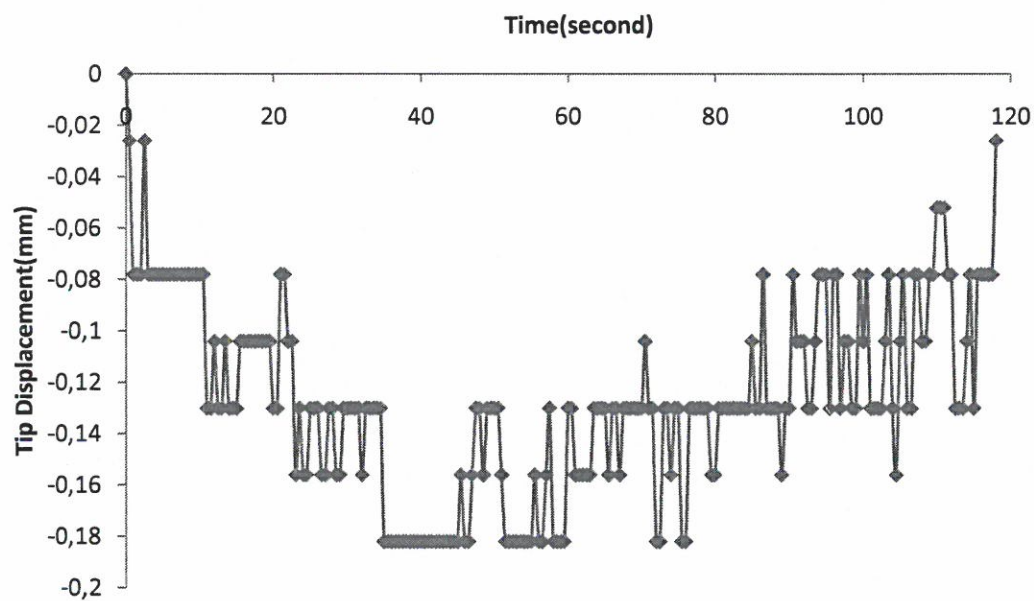


Figure 3.43 The time evolution of the tip displacement (time response) of Cel-Cl-DMAC(7v)

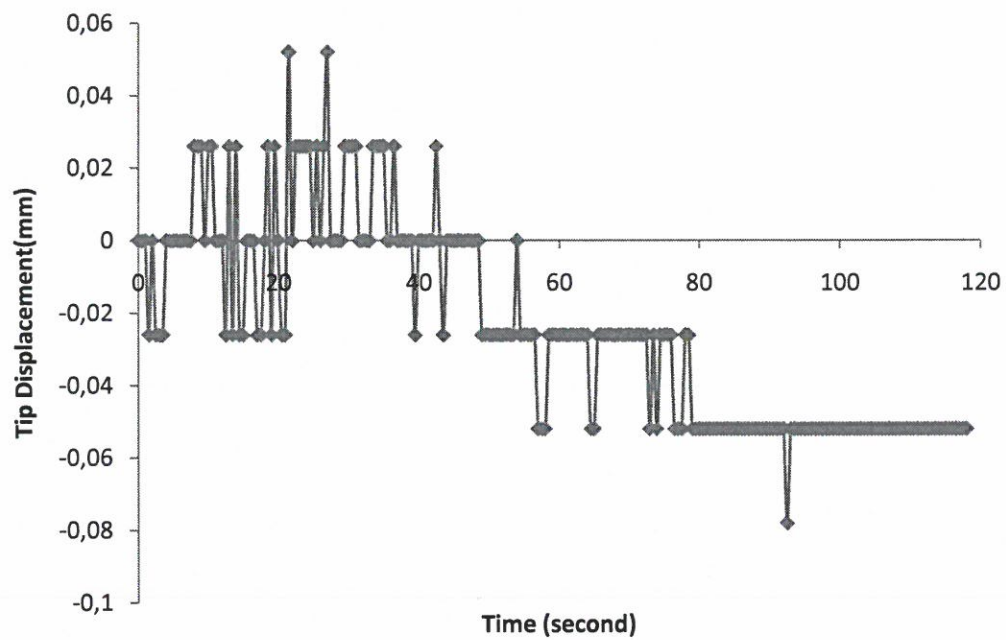


Figure 3.44 The time evolution of the tip displacement (time response) of Cel-Cl-DMAC(-7v)

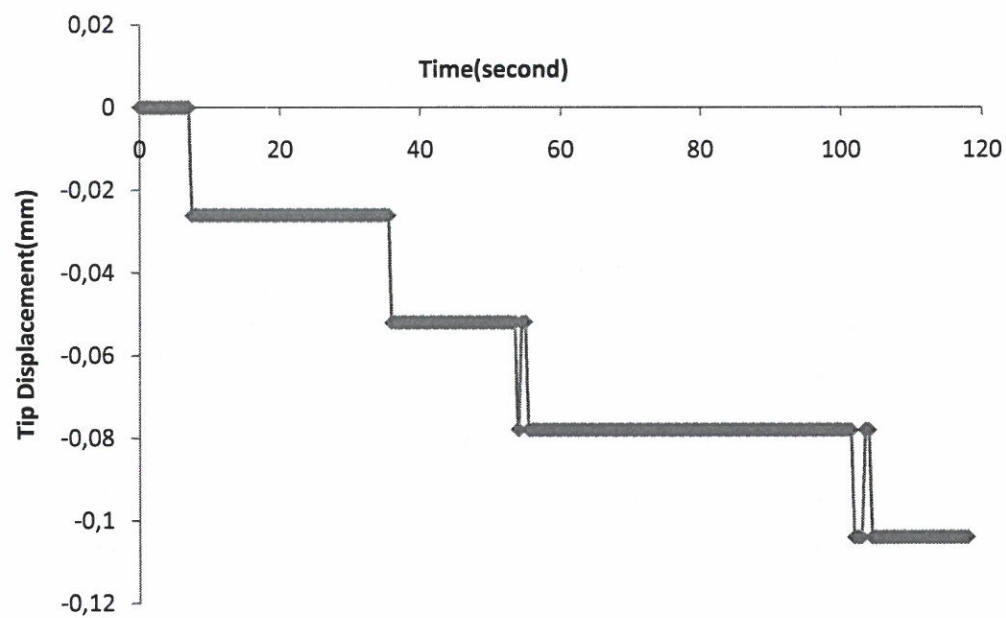


Figure 3.45 The time evolution of the tip displacement (time response) of Cel-Cl-DMAC-0.1Gr(5v)

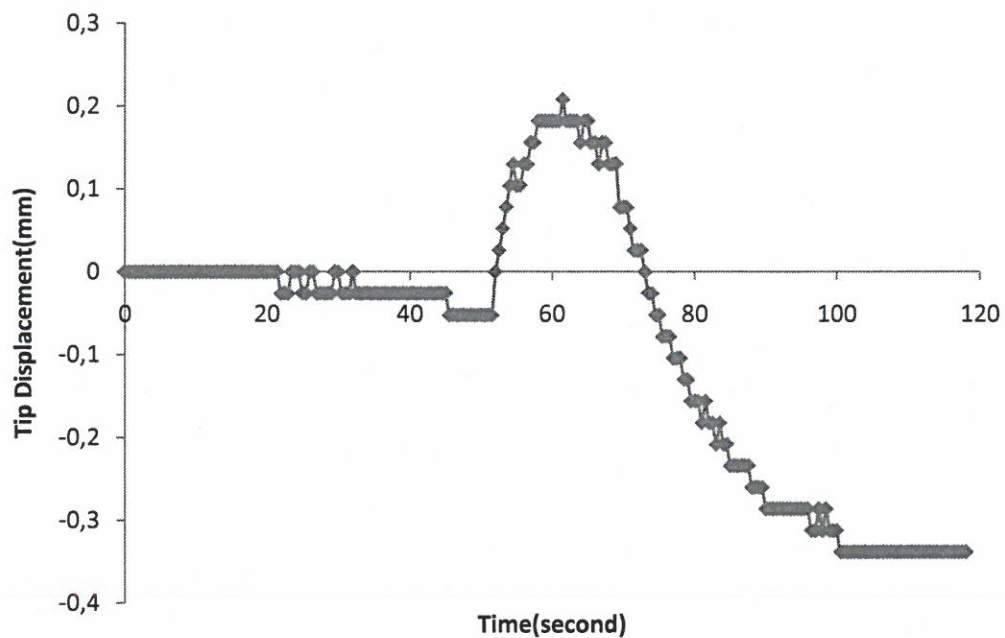


Figure 3.46 The time evolution of the tip displacement (time response) of Cel-Cl-DMAC-0.1Gr(-5v)

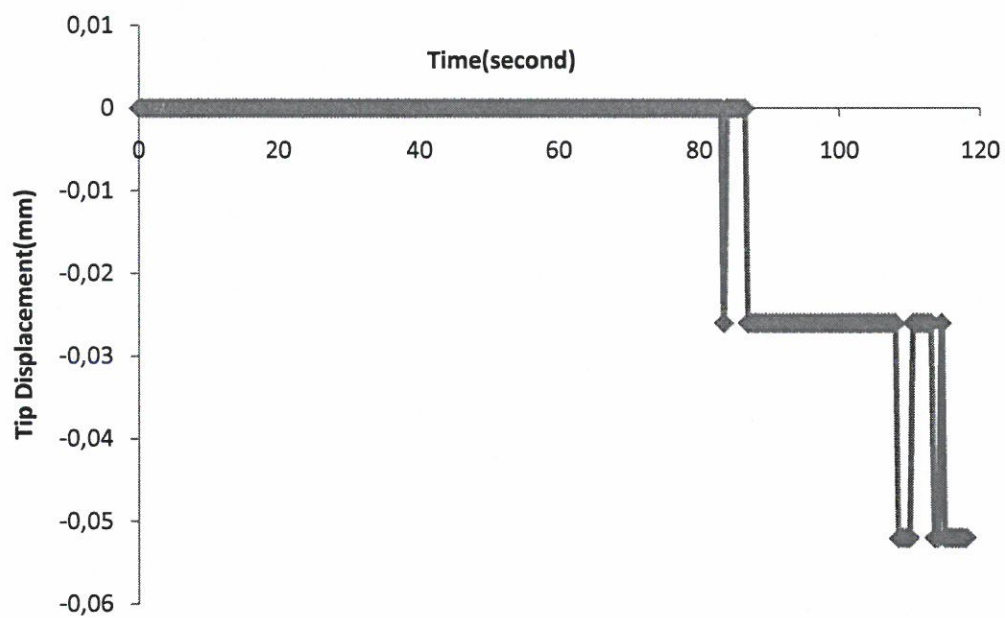


Figure 3.47 The time evolution of the tip displacement (time response) of Cel-Cl-DMAC-0.1Gr(7v)

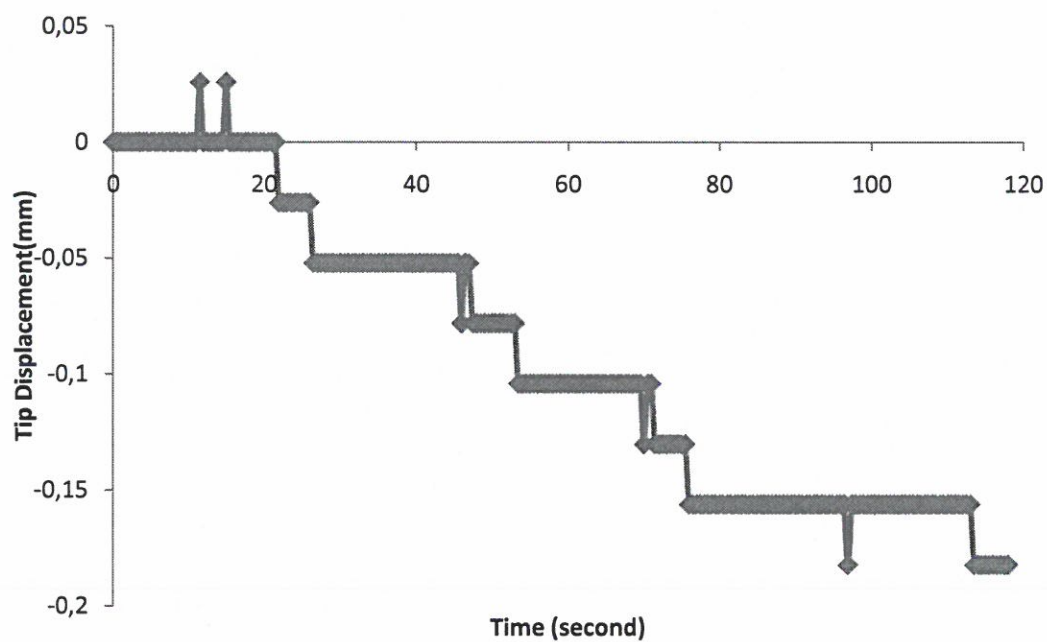


Figure 3.48 The time evolution of the tip displacement (time response) of Cel-Cl-DMAC-0.1Gr(-7v)

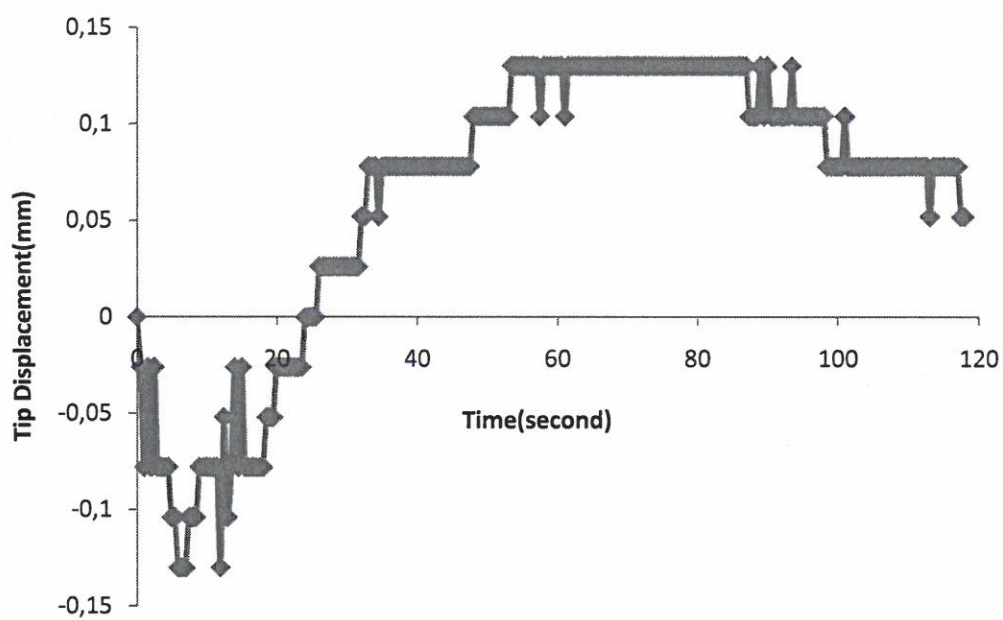


Figure 3.49 The time evolution of the tip displacement (time response) of Cel-Cl-DMAC-0.25Gr(7v)

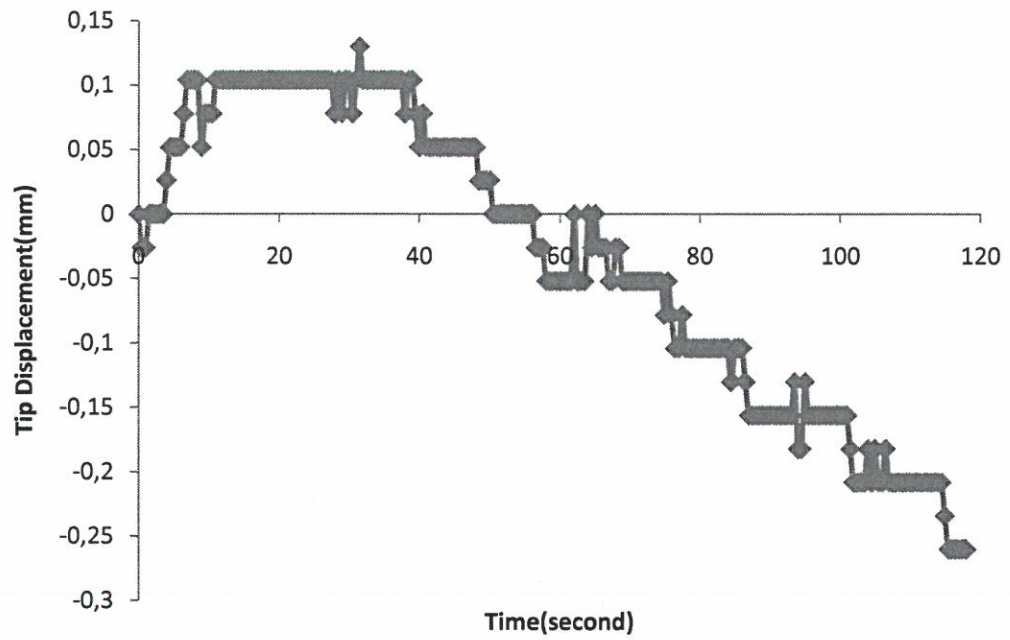


Figure 3.50 The time evolution of the tip displacement (time response) of Cel-Cl-DMAC-0.25Gr(-7v)

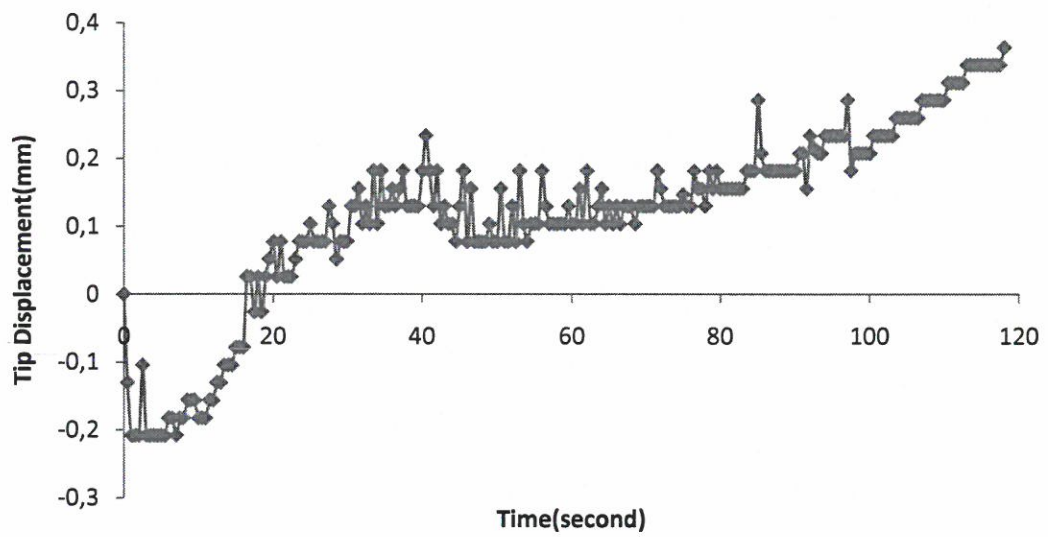


Figure 3.51 The time evolution of the tip displacement (time response) of Cel-Cl-DMAC-0.375Gr(3v)

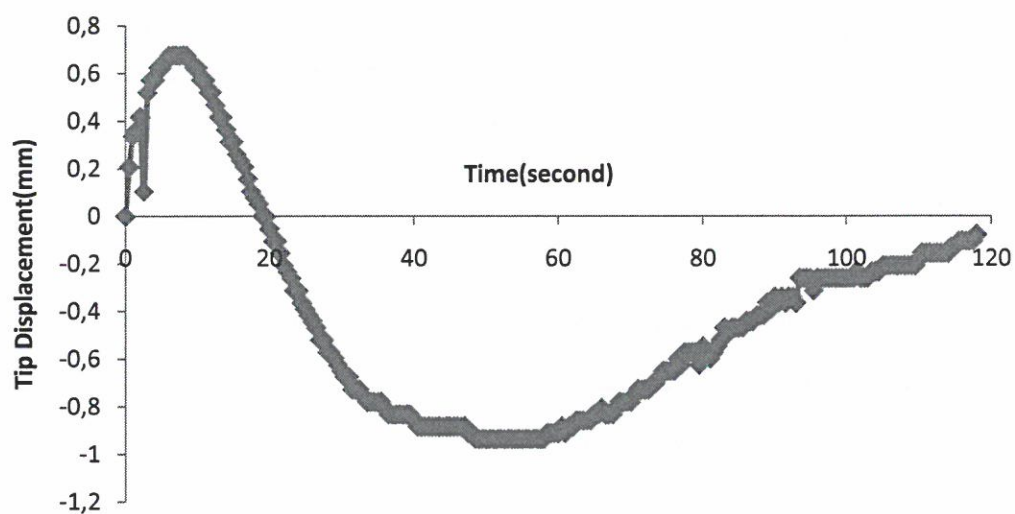


Figure 3.52 The time evolution of the tip displacement (time response) of Cel-Cl-DMAC-0.375Gr (-3v)

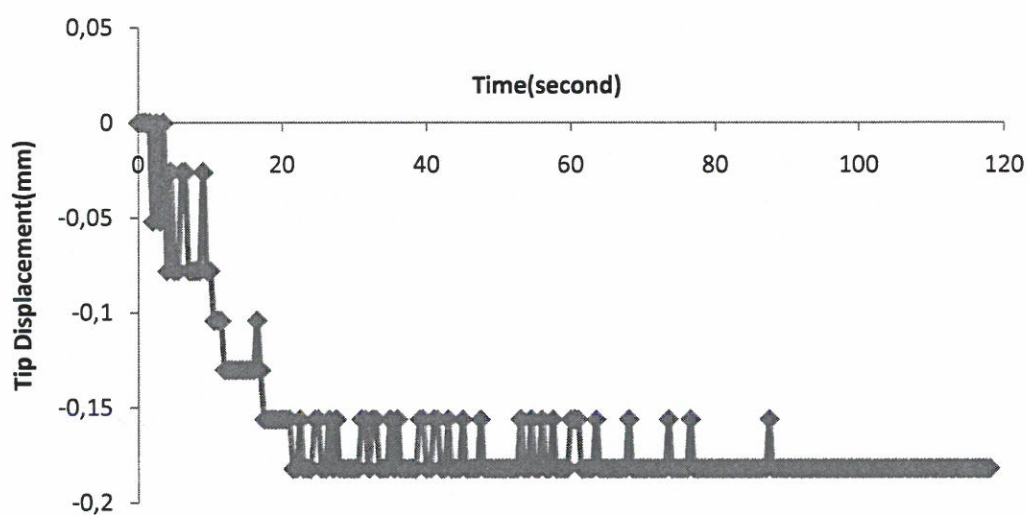


Figure 3.53 The time evolution of the tip displacement (time response) of Cel-Cl-DMAC-0.375Gr(5v)

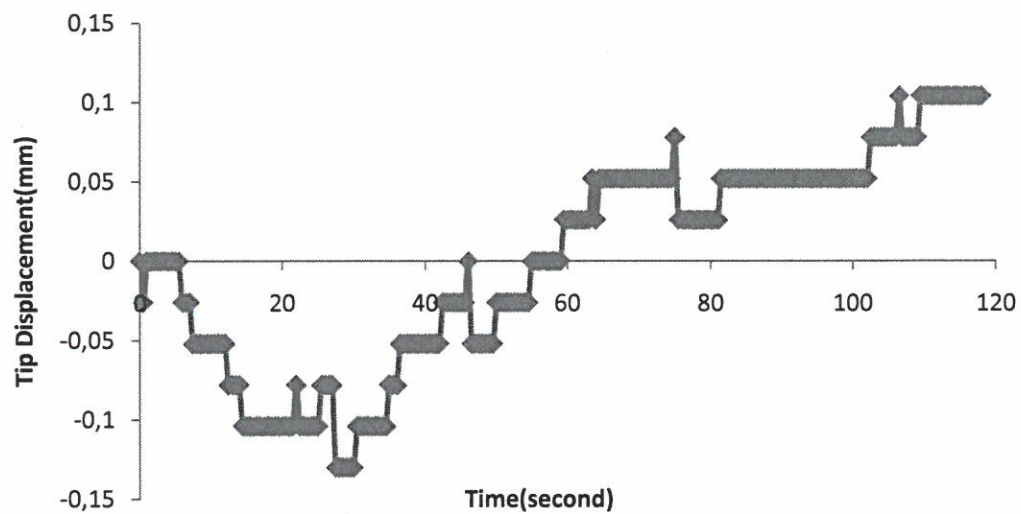


Figure 3.54 The time evolution of the tip displacement (time response) of Cel-Cl-DMAC-0.375Gr (-5v)

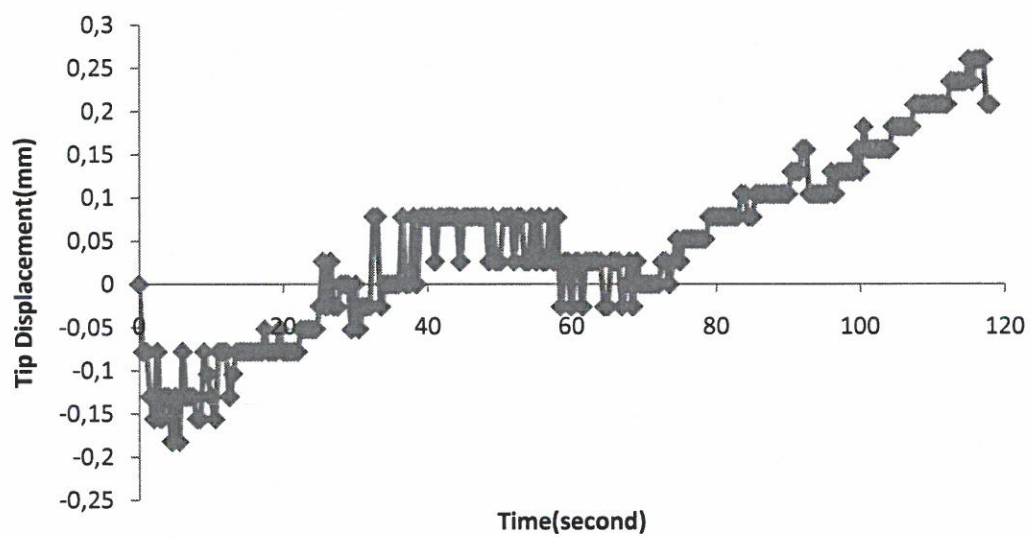


Figure 3.55 The time evolution of the tip displacement (time response) of Cel-Cl-DMAC-0.375Gr(7v)

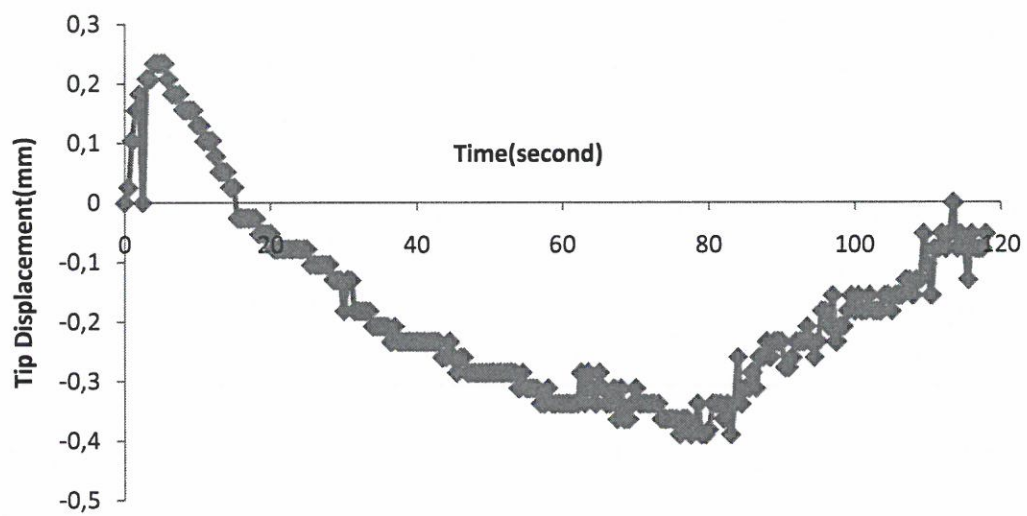


Figure 3.56 The time evolution of the tip displacement (time response) of Cel-Cl-DMAC-0.375Gr (-7v)

CHAPTER FOUR

CONCLUSIONS

Cellulose was dissolved in an ionic liquid, butyl methyl imidazolium chloride and dimethylacetamide at 100°C and cellulose-based films were successfully produced. In order to improve electromechanical properties of cellulose based films, graphene at different ratios (0.1%, 0.25%, 0.375% and 0.5%) was dispersed in this solution and new films were produced by means of a solution casting method.. The characterization of this film was conducted by FTIR, TGA, XRD, SEM, electrical conductivity and tensile properties. The surfaces of the Cel-Cl-DMAC and Cel-Cl-DMAC-Gr films were gold- coated with a thin gold leaf so as to produce electro-active actuators. Actuation performances of Cel-Cl-DMAC-0.1Gr, Cel-Cl-DMAC-0.25Gr, Cel-Cl-DMAC-0.375Gr, and Cel-Cl-DMAC-0.5Gr actuators were investigated by way of maximum tip displacements and time constants. Based on the experimental results, the following points can be concluded:

- From FTIR of the Cel-Cl-DMAC film, new bands were remarked. These new bands corresponding to 1569 (amide II bands), 3142, 3086, 2957 and 2858 cm^{-1} showed the existence of ionic liquid and DMAC in film structure. After Gr was loaded into Cel-Cl-DMAC, the intensity of -OH band altered slightly.
- Significant diminishment in thermal property of Cel-Cl-DMAC was obtained after graphene loading to Cel-Cl-DMAC. The final decomposition temperature decreased considerably (from 353°C for Cel-Cl-DMAC to 318°C for Cel-Cl-DMAC-0.375Gr film).
- While XRD pattern of Cellulose has three diffraction peaks, after Cel was dissolved in BMIMCl and DMAC, the film has one diffraction peak which is the main characteristic peak at 2θ angle (22.8°). The CI of cellulose is 0.81. When graphene was loaded into Cel-Cl-DMAC, the CI of Gr loaded Cel-Cl-DMAC changed slightly for Cel-Cl-DMAC-0.1Gr, Cel-Cl-DMAC-0.25Gr, and Cel-Cl-DMAC-0.375Gr. The crystallite size of Cel was obtained to be 6.15 nm, however,

after dissolution of cellulose in IL, crystallite size decreased to 1.18 nm. After graphene was loaded into Cel-Cl-DMAC, the crystallite size of Gr loaded Cel-Cl-DMAC decreased slightly (from 0.78 to 0.70).

- According to SEM images of Cel-Cl-DMAC, cellulose particles were disorderly dispersed in both micro-dimension size and in nano-dimension size. This size is 50-200 nm. As shown in SEM images of Cel-Cl-DMAC-0.1Gr, Cel-Cl-DMAC-0.25Gr and Cel-Cl-DMAC-0.375Gr, graphene sheets cannot be seen in cellulosic film.

- Significant increment in mechanical properties of Cel-Cl-DMAC was obtained after graphene loading into Cel-Cl-DMAC. Both Young's modulus and tensile strength of Cel-Cl-DMAC-0.1Gr, Cel-Cl-DMAC-0.25Gr, and Cel-Cl-DMAC-0.375Gr films were obtained to be higher than that of Cel-Cl-DMAC.. However, for Cel-Cl-DMAC-0.5Gr's Young's modulus and tensile strength are lower than those of Cel-Cl-DMAC-0.375Gr. When both sides of the films were coated on gold film, both Young's modulus and tensile strength of the films increased by 16-30%

- As graphene was dispersed in Cel-Cl-DMAC, electrical conductivity of the Cel-Cl-DMAC films was increased. Increment in electrical conductivity values may be attributed to combinations of highly conductive graphene in the Cel-Cl-DMAC.

- The observations on electromechanical characteristics show that there is a nonlinear relationship between the content of Graphene and electroactive characteristics of IPMC actuators: the maximum tip displacement and time constant. For $3V_{DC}$, Cel-Cl-DMAC-0.25Gr has the greatest maximum tip displacement for all actuators. But For Cel-Cl-DMAC-0.5Gr when voltage was rised to 5V and 7V, not only the maximum tip displacement but also time constant decreased.

REFERENCES

- Agarwal, V., Huber, G. W., Conner, W. C. ,& Auerbach, S. M. (2011). Simulating infrared spectra and hydrogen bonding in cellulose I β at elevated temperatures. *The Journal of Chemical Physics*, 135, 134506.
- Akle, B. J., Bennett, M. D., & Leo, D. J. (2006). High-strain ionomeric–ionic liquid electroactive actuators. *Sensors and Actuators A: Physical*, 126(1), 173-181.
- Burchell, T. D. (1999). *Carbon materials for advanced technologies*, Access Online via Elsevier.
- Chen, H. Z., Wang, N. ,& Liu, L. Y. (2012). Regenerated cellulose membrane prepared with ionic liquid 1-butyl-3-methylimidazolium chloride as solvent using wheat straw. *Journal of Chemical Technology and Biotechnology*, 87(12), 1634-1640.
- Chen, Z., Um, T. I. ,& Bart-Smith, H. (2011). A novel fabrication of ionic polymer–metal composite membrane actuator capable of 3-dimensional kinematic motions. *Sensors and Actuators A: Physical*, 168(1), 131-139.
- Chieng, B. W., Ibrahim, N. A., Wan Yunus, W. M. Z., Hussein, M. Z. ,& Silverajah, V. (2012). Graphene Nanoplatelets as Novel Reinforcement Filler in Poly (lactic acid)/Epoxidized Palm Oil Green Nanocomposites: Mechanical Properties. *International Journal of Molecular Sciences*, 13(9), 10920-10934.
- Du, F.-P., Tang, C.-Y., Zhou, X.-P. ,& Xie, X.-L. (2011). Fabrication of an ionic polymer-carbon nanotube composite for a new configurative actuator. *Journal of Composite Materials*, 45(20), 2055-2060.
- Earle, M. J. & Seddon, K. R. (2000). Ionic liquids. Green solvents for the future. *Pure and Applied Chemistry*, 72(7), 1391-1398.

- Enikov, E. T. & Seo, G. S. (2005). Analysis of water and proton fluxes in ion-exchange polymer-metal composite (IPMC) actuators subjected to large external potentials. *Sensors and Actuators A: Physical*, 122(2), 264-272.
- Fang, B.-K., Ju, M.-S. & Lin, C.-C. K. (2007). A new approach to develop ionic polymer-metal composites (IPMC) actuator: Fabrication and control for active catheter systems. *Sensors and Actuators A: Physical*, 137(2), 321-329.
- Fang, B.-K., Lin, C.-C. K. & Ju, M.-S. (2010). Development of sensing/actuating ionic polymer-metal composite (IPMC) for active guide-wire system. *Sensors and Actuators A: Physical*, 158(1), 1-9.
- Ferrari, A. & Robertson, J. (2000). Interpretation of Raman spectra of disordered and amorphous carbon. *Physical Review B*, 61(20), 14095.
- Geng, D., Yang, S., Zhang, Y., Yang, J., Liu, J., Li, R. et al. (2011). Nitrogen doping effects on the structure of graphene. *Applied Surface Science*, 257(21), 9193-9198.
- Goenka, S., Sant, V. ,& Sant, S. (2014). Graphene-based nanomaterials for drug delivery and tissue engineering. *Journal of Controlled Release*, 173, 75-88.
- Han, D., Yan, L., Chen, W., Li, W., & Bangal, P. (2011). Cellulose/graphite oxide composite films with improved mechanical properties over a wide range of temperature. *Carbohydrate Polymers*, 83(2), 966-972.
- Hazarika, M. & Jana, T. (2013). Graphene nanosheets generated from sulfonated polystyrene/graphene nanocomposite. *Composites Science and Technology*, 87, 94-102.
- He, Q., Yu, M., Li, Y., Ding, Y., Guo, D., Dai, Z. et al. (2012). Investigation of ionic polymer metal composite actuators loaded with various tetraethyl orthosilicate contents. *Journal of Bionic Engineering*, 9(1), 75-83.

- Jeon, J.-H., Yeom, S.-W. & Oh, I.-K. (2008). Fabrication and actuation of ionic polymer metal composites patterned by combining electroplating with electroless plating. *Composites Part A: Applied Science and Manufacturing*, 39(4), 588-596.
- Jo, C., Pugal, D., Oh, I.-K., Kim, K. J. ,& Asaka, K. (2013). Recent advances in ionic polymer-metal composite actuators and their modeling and applications. *Progress in Polymer Science*.
- Johnson, K. E. (2007). What's an ionic liquid? *Interface-Electrochemical Society*, 16(1), 38-41.
- Jung, J.-H., Jeon, J.-H., Sridhar, V. ,& Oh, I.-K. (2011). Electro-active graphene–Nafion actuators. *Carbon*, 49(4), 1279-1289.
- Kadokawa, J.-i., Murakami, M.-a. & Kaneko, Y. (2008). A facile preparation of gel materials from a solution of cellulose in ionic liquid. *Carbohydrate Research*, 343(4), 769-772.
- Kim, J. (2007). Cellulose as a smart material. *Cellulose: Molecular and Structural Biology*, Springer.
- Kim, J. S. & Cai, Y. P. (2012). Study of characteristics of cellulose based electro-active material. *American Journal of Sciences Developments*, 3, 6-10.
- Kim, K. J. & Tadokoro, S. (2007). *Electroactive polymers for robotics applications: Artificial muscles and sensors*, Springer.
- Kirchner, B. (2009). *Ionic liquids*, Springer.
- Kuila, T., Bose, S., Hong, C. E., Uddin, M. E., Khanra, P., Kim, N. H. et al. (2011). Preparation of functionalized graphene/linear low density polyethylene composites by a solution mixing method. *Carbon*, 49(3), 1033-1037.

- Kunchornsup, W. & Sirivat, A. (2010). Effects of crosslinking ratio and aging time on properties of physical and chemical cellulose gels via 1-butyl-3-methylimidazolium chloride solvent. *Journal of Sol-Gel Science and Technology*, 56(1), 19-26.
- Lee, J.-W. & Yoo, Y.-T. (2011). Preparation and performance of IPMC actuators with electrospun Nafion®–MWNT composite electrodes. *Sensors and Actuators B: Chemical*, 159(1), 103-111.
- Lee, K. S., Jeon, B. J. ,& Cha, S. W. (2010). Performance enhancement of an ionic polymer metal composite actuator using a microcellular foaming process. *Smart Materials and Structures*, 19(6), 065029.
- Li, W., Jin, A., Liu, C., Sun, R., Zhang, A., Kennedy, J. et al.(2009). Homogeneous modification of cellulose with succinic anhydride in ionic liquid using 4-dimethylaminopyridine as a catalyst. *Carbohydrate Polymers*, 78(3), 389-395.
- Liu, D.-t., Xia, K.-f., Cai, W.-h., Yang, R.-d., Wang, L.-q., Wang, B. et al.. (2012). Investigations about dissolution of cellulose in the 1-allyl-3-alkylimidazolium chloride ionic liquids. *Carbohydrate Polymers*, 87(2), 1058-1064.
- Liu, J., Cui, L. & Losic, D. (2013). Graphene and graphene oxide as new nanocarriers for drug delivery applications. *Acta Biomaterialia*, 9(12), 9243-9257.
- Mahmoudian, S., Wahit, M. U., Imran, M., Ismail, A. ,& Balakrishnan, H. (2012). A facile approach to prepare regenerated cellulose/graphene nanoplatelets nanocomposite using room-temperature ionic liquid. *Journal of Nanoscience and Nanotechnology*, 12(7), 5233-5239.
- Merck (2014). Retrieved July 15 , 2014 from , https://www.merckmillipore.com/TR/en/product/N%2CN-Dimethylacetamide,MDA_CHEM-803235

- Nature (2010). Retrieved December 26, 2013 from http://www.nature.com/nphys/journal/v7/n12/images_article/nphys2166-f1.jpg
- Oh, S. Y., Yoo, D. I., Shin, Y. & Seo, G. (2005). FTIR analysis of cellulose treated with sodium hydroxide and carbon dioxide. *Carbohydrate Research*, 340(3), 417-428.
- Paquette, J. W. & Kim, K. J. (2004). Ionomeric electroactive polymer artificial muscle for naval applications. *Oceanic Engineering, IEEE Journal of*, 29(3), 729-737.
- Pierson, H. O. (1993). *Handbook of carbon, graphite, diamond, and fullerenes: properties, processing, and applications*. New Jersey: Noyes Publications Park Ridge.
- Seki, Y., Sarikanat, M., Sever, K. & Durmuşkahya, C. (2013). Extraction and properties of *Ferula communis* (chakshir) fibers as novel reinforcement for composites materials. *Composites Part B: Engineering*, 44(1), 517-523.
- Sescousse, R., Gavillon, R. & Budtova, T. (2011). Aerocellulose from cellulose-ionic liquid solutions: Preparation, properties and comparison with cellulose-NaOH and cellulose-NMMO routes. *Carbohydrate Polymers*, 83(4), 1766-1774.
- Shahinpoor, M., Bar-Cohen, Y., Simpson, J. & Smith, J. (1998). Ionic polymer-metal composites (IPMCs) as biomimetic sensors, actuators and artificial muscles-a review. *Smart Materials and Structures*, 7(6), R15.
- Shahinpoor, M. & Kim, K. J. (2005). Ionic polymer-metal composites: IV. Industrial and medical applications. *Smart Materials and Structures*, 14(1), 197.
- Sigmaaldrich(2013). Retrieved December 26, 2013 from <http://www.sigmaaldrich.com/catalog/product/fluka/55509?lang=en®ion=TR>

- Sowmiah, S., Srinivasadesikan, V., Tseng, M.-C. & Chu, Y.-H. (2009). On the chemical stabilities of ionic liquids. *Molecules*, 14(9), 3780-3813.
- Stefanescu, C., Daly, W. H. ,& Negulescu, I. I. (2012). Biocomposite films prepared from ionic liquid solutions of chitosan and cellulose. *Carbohydrate Polymers*, 87(1), 435-443.
- Takegawa, A., Murakami, M.-a., Kaneko, Y. & Kadokawa, J.-i. (2010). Preparation of chitin/cellulose composite gels and films with ionic liquids. *Carbohydrate Polymers*, 79(1), 85-90.
- Vitz, J., Erdmenger, T., Haensch, C. & Schubert, U. S. (2009). Extended dissolution studies of cellulose in imidazolium based ionic liquids. *Green Chemistry*, 11(3), 417-424.
- Wang, Y., Shi, Z., Fang, J., Xu, H. & Yin, J. (2011). Graphene oxide/polybenzimidazole composites fabricated by a solvent-exchange method. *Carbon*, 49(4), 1199-1207.
- Wasserscheid, P. & Welton, T. (2008). *Ionic liquids in synthesis*, Wiley Online Library.
- Wendler, F., Todi, L.-N. & Meister, F. (2012). Thermostability of imidazolium ionic liquids as direct solvents for cellulose. *Thermochimica Acta*, 528, 76-84.
- Yip, J., Ding, F., Yick, K.-L., Yuen, C.-W. M., Lee, T.-T., Choy, W.-H. et al. (2012). Tunable carbon nanotube ionic polymer actuators that are operable in dry conditions. *Sensors and Actuators B: Chemical*, 162(1), 76-81.
- Wikimedia Commons (2009). Retrieved December 26 2013 from http://commons.wikimedia.org/wiki/File:Carbon_lattice_diamond.png

- Zadegan, S., Hossainipour, M., Ghassai, H., Rezaie, H. & Naimi-Jamal, M. (2010). Synthesis of cellulose–nanohydroxyapatite composite in 1-n-butyl-3-methylimidazolium chloride. *Ceramics International*, 36(8), 2375-2381.
- Zadegan, S., Hosainipour, M., Rezaie, H., Ghassai, H. & Shokrgozar, M. (2011). Synthesis and biocompatibility evaluation of cellulose/hydroxyapatite nanocomposite scaffold in 1- n-allyl-3-methylimidazolium chloride. *Materials Science and Engineering: C*, 31(5), 954-961.
- Zhang, S., Lu, X., Zhou, Q., Li, X., Zhang, X., Li, S. et al. (2009). *Ionic Liquids: Physicochemical Properties*, Access Online via Elsevier.