CHAPTER 1

INTRODUCTION

1.1 Project Background

In the face of great environmental adversities, ‘green chemistry’ has immersed increasingly important day by day. Ionic liquids have overwhelming potential to be posited as solvents for industrial applications to be more environmental friendly. Ionic liquids are basically solvents that can be applied for various applications. One of the most popular advantage of ionic liquids over volatile organic compounds (VOCs) as solvents is the low vapour pressure demonstrated by ionic liquids.

Epoxy or polyepoxide is a thermosetting polymer formed from reaction between a resin and harderner (curing agent). Nowadays, epoxy coating is applied widely as corrosion preventive application. Storage tanks and pipes in the industry apply epoxy coating to avoid or slowdown corrosion problem in many cases. Epoxy coatings are normally cured in room temperature condition. However in some occasions, several epoxy coatings are cured in the oven at high temperature.

Currently, the study on the effects of ionic liquids on epoxy coating has not been explored. Extensive experimental studies such as absorption test, Fourier Transform Infrared (FTIR) test, pull-off adhesion test and Scanning Electron Microscope (SEM) will be conducted to discover the unknown effects of ionic liquids on epoxy coating.

1.2 Problem Statement

Seeing that ionic liquids have vast potential to be commercialized, it is not impossible to be applied extensively for petrochemical industry in the years to come. Ultimately, these ionic liquids will need to be stored in storage tanks or transported via pipes. These tanks and pipes normally utilize epoxy coating as corrosion protection mechanism. The problem is we do not know whether these ionic liquids react, degrade or interact with the epoxy coating. No such research or study has been conducted to date. Therefore, it is very important to establish the effects of ionic liquids on epoxy coating first before it is being commercialize widely. If there are negative effects discovered, we might want to replace epoxy coating with another type of coating material if we want to utilize ionic liquid in our petrochemical industry. Else, ionic liquid can be applied at ease.

1.3 Objectives and Scope of Study

While the goal of the project is to establish the effects of ionic liquids on epoxy coating, the objectives of this project are as following:

1) To select three room temperature ionic liquids that are capable to function as desulphurization agent.
2) To prepare epoxy coatings and epoxy bars.
3) To study the ionic liquids' interaction with the epoxy coating and epoxy bar.

This project will be focusing mainly on ionic liquids and epoxy coating. The effects of ionic liquids on epoxy coating will be observed through multiple experiments such as absorption test, Fourier Transform Infrared (FTIR), Scanning Electron Microscope (SEM), and pull-off adhesion test.

1.4 Relevance of the Project

This project is pretty much relevant to the industry since ionic liquids have big potential to be exploited further in the coming future. On the other hand, epoxy coating has been applied extensively in various industrial applications mainly as corrosion protection measure. However, no research or study has been conducted so far to establish the effects of ionic liquids exposure to epoxy coating. This project will play a vital role to discover and establish such effects in the future before ionic liquids can be commercialized fully in the industry.

1.5 Feasibility of the Project

This project is feasible within the time framework because it involves primarily experimental based activities that are fully equipped in the university. Furthermore, all the resources needed for this project are mostly available in the university. Thus it is not necessary to consume time for travelling to other locations in order to get the necessary resources or equipments usage.

CHAPTER 2

LITERATURE REVIEW

The effect of ionic liquids on epoxy coating is the main attention of this project. Therefore, the objective of this literature review is to gain as much information as possible with regard to ionic liquid and epoxy since those are the subjects of this project. This literature review will also highlight the theory for methodology required for the research project. Summarisation is done at the end of the literature review.

2.1 Ionic Liquid

2.1.1 Introduction to Ionic Liquid

Ionic liquid is easily defined as salt in liquid form consisting of ion and ion pairs [1]. Ionic liquids have received escalating attention recently in basic research because of its vast potential as a 'greener' replacement for volatile organic solvents. Room Temperature Ionic liquids (RTILs) are salts that normally melt at low temperature, most likely ambient temperature.

Because ionic liquids are composed of only ions, they show very high ionic conductivity, nonvolatility, and nonflammability [2]. In many cases, the use of ionic liquids has been considered as the key element in the design of more environmentally benign methods for separations. These solvents (ionic liquids) display several properties that make them feasible as a potential basis for 'greener' separation processes, such as negligible vapour pressure, a wide liquid range, and good thermal stability [3].

Currently, most of the attention in ionic liquids is centred on the design of new solvents. While the development of 'new solvents' has led the direction of possible applications of ionic liquids, there is more potential for development in electrochemical applications as well [2]. Shown below are the potential applications of ionic liquid.

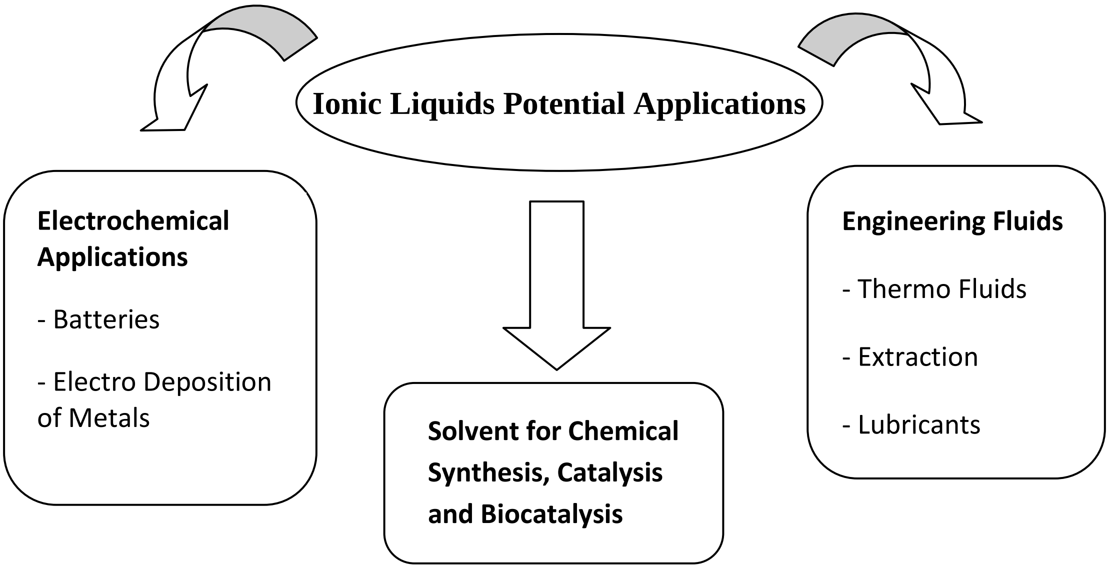


Figure 2.1: Potential Applications of Ionic Liquids [3]

2.1.2 Room Temperature Ionic Liquid (RTIL)

Room temperature ionic liquids (RTILs) are basically organic salts which exist in liquid form at ambient temperature. It normally composed of relatively large asymmetric organic cations and inorganic or organic anions. Due to the impressive characteristics of RTILs such as insignificant vapour pressure and solubility of a wide range of organic and inorganic compounds, they have generated a lot of interest in the industry as ‘green’ solvents [14]. One of the examples of RTIL is 1-alkyl-3-methylimidazolium.

2.1.3 Imidazolium Salts

Imidazole is defined as organic compounds of the heterocyclic series which consists of three carbon atoms and two nitrogen atoms at nonadjacent positions. The formula of imidazole is $C_3H_4N_2$ [15]. Shown below is the molecular structure of imidazole.

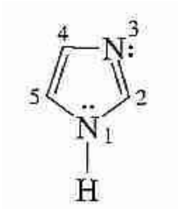


Figure 2.2: Molecular Structure of Imidazole [16]

Imidazolium salts on the other hand are salts that have cation of imidazole, for example imidazolium chloride. These salts are formed from the substitution at nitrogen of imidazole with an anion [18]. These salts have been used extensively in ionic liquids application because of their ability to be infinitely recycled and remain as solvent/liquid at room temperature, making them excellent green solvents [17]. Salts where imidazole exists as an anion are also possible, these salts are known as imidazolide salts, for example sodium imidazolide [18].

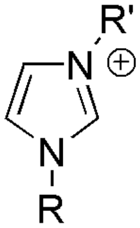


Figure 2.3: Molecular Structure of Imidazolium Salt [19]

Imidazolium salt also has shown good potential as desulphurization agent presumably due to its similarity in structure to the rings of sulphur compounds [22].

2.1.4 Desulphurisation of Gasoline and Diesel Using Ionic Liquids

Deep desulfurization of gasoline and diesel is becoming more important in the recent years due to the environmental regulation on the limit of sulphur in the fuels. The extraction of sulphur can be carried out by some molecular solvents such as polyalkylene glycol, polyalkylene glycol ether, pyrrolidones, imidazolidinones, and pyrimidinones [23]. Nonetheless, the extraction performance was just average, and sometimes their solubility in fuel or vice versa is noticeably leading to a cross-contamination. On the other hand, ionic liquid (IL) seems more competitive considering the facts [23]:

1) It is environmental friendly and designable.
2) It is immiscible with fuels and therefore free of cross-contamination.
3) It is non-volatile and remains stable thermally over a wide range of temperature; consequently the used IL can be regenerated by distillation.
4) Its conductance makes it more applicable for the selection of regeneration methods for the used IL solvent.
5) Many ILs (e.g. [BMIM]Cl/AlCl3, [BMIM][BF4], [BMIM][PF6], [BMIM]-[OcSO4], [MMIM][DMP],4-6 [BMIM][Cu2Cl3], etc.) show desulfurization potential to a different degree.

Extractive desulphurization process will be more effective if the ILs used are nontoxic, chemically stable to moisture and air, and not expensive for commercial application. Taking into consideration these requirements, the imidazolium-based phosphoric ILs are advantageous because of its easy manufacturing in commercial scale [23].

Comment: Ionic liquids have shown promising potential in many industrial applications, not only as excellent solvent but also as desulphurization agent. Based on the literature review done above, imidazolium based ionic liquids show big potential as desulphurization agent. Therefore, imidazolium based ionic liquids will be selected as the main specimens for the experiment with epoxy coating.

2.2 Epoxy Coating

2.2.1 Introduction to Epoxy Coating

An epoxy coating or paint is a protective material made from epoxy-based resin [8]. Epoxy which is also known as polyepoxide is a thermosetting epoxide polymer that is formed from two different chemicals, generally ‘resin’ and ‘hardener’. The resin usually consists of monomers or short chain polymer that is commonly produced from the reaction between epichlorohydrin and bisphenol A, although the later can be replaced with other chemicals such as bisphenol F and phenolic novalac [4][5]. The typical structure of epoxy is shown below.

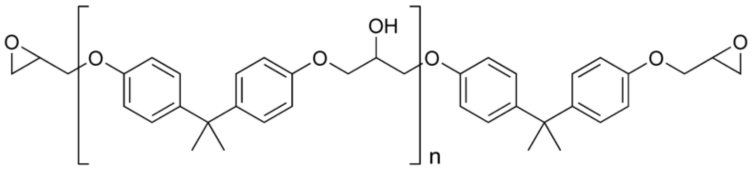


Figure 2.4: Structure of Epoxy Prepolymer [20]

Apart from the resin, the ‘hardener’ or curing agent is equally important to produce an epoxy. The ‘hardener’ normally consists of polyamine monomers such as polyamide, aromatic amide, and amidoamine [5]. When these compounds are mixed together, the amine groups react with the epoxide groups to form a covalent bond. Each NH group will react with an epoxide group, resulting in polymer that is heavily crosslinked, which is rigid and strong [6][7]. Shown in the next page is the structure of m-xylylenediamine (m-XDA), an example of polyamine monomer.

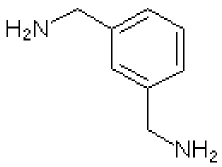


Figure 2.5: Structure pf m-xylenediamine (m-XDA) [21]

Different combinations of resins and curing agent will result in different properties of epoxies [5]. Generally, epoxies are well known for their impressive adhesion and resistance against corrosive chemicals, heat, and ultra-violet light [8]. Therefore, it is widely used as coating/protective material to prevent or minimise corrosion problems in storage tanks and pipes for transportation purposes.

2.2.2 Corrosion Stability of Epoxy Coating

An experiment was conducted to study the corrosion stability of epoxy coatings on aluminium pretreated by vinyltriethoxysilane (VTES). In this experiment, the electrochemical properties and adhesion of epoxy coating are observed after it was pretreated with vinyltriethoxysilane [26]. Based on the experiment, it was observed that the pore resistance of the epoxy coating decreases over time after its exposure to NaCl solution. However it was notable that the pretreated epoxy coating showed greater pore resistance if it’s treated with greater concentration of VTES film. This can be seen clearly on Nyquist plots shown below as the result of electrochemical impedance spectroscopy (EIS) experiment conducted [26].

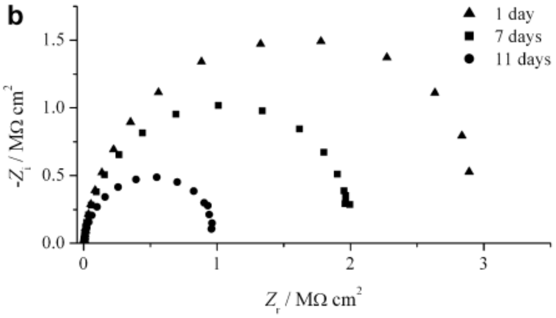


Figure 2.6: Epoxy coatings on aluminum pretreated by VTES films on the first 11 days of exposure to 3% NaCl [26]

From that experiment as well, it was observed that the adhesion strength of the coating dropped at least 30% from its original adhesion strength after exposure of 20 days to 3% NaCl solution [26].

Comment: Even though epoxy coating showed good protective properties, it was proven that long exposure of epoxy coating to ionic compounds will significantly drop the corrosion resistance. In addition, the adhesion strength of the epoxy coating also dropped after its long exposure to corrosive environment of ionic compounds. This information will further strengthen the probability of ionic liquids attack on the epoxy coating.

2.3 Absorption in Polymeric Materials

One of the famous absorption studies in polymeric materials is the water absorption. Water absorption is defined as "the amount of water absorbed by a composite material when immersed in water for a stipulated period of time, and also the ratio of the weight of water absorbed by a material, to the weight of the dry materials. All organic polymeric materials will absorb moisture to some extent resulting in swelling, dissolving, leaching, plasticizing and/or hydrolyzing, events which can result in discoloration, embrittlement, loss of mechanical and electrical properties, lower resistance to heat and weathering and stress cracking." [9]

For the water absorption test, the samples are dried and cooled down prior to the test. Right away upon cooling, the samples are weighed. The material is then immersed in water normally at temperature of 23°C for 24 hours or until equilibrium. Samples are then taken out, dried, and weighed [10]. Percentage of water absorption is calculated using the following equation:

$$\boxed{\%\ \text{Absorption} = [(\text{wet weight} - \text{dry weight})/\text{dry weight}] \times 100}$$

Equation 2.1

Comment: Although the above methodology is done for the testing of water absorption, it is not impossible to apply it in determining the percentage of ionic liquid absorption in epoxy. Instead of being immersed in water, the samples could be immersed in ionic liquid to observe the increment of weight in the samples if there is any.

2.4 Scanning Electron Microscope (SEM)

Scanning Electron Microscope (SEM) is a type of microscope that applies electrons to form an image instead of using light. Scanning electron microscopes have expanded new areas of study in the medical and physical science communities since its development in the early 1950's. It allows researchers and scientist to examine a much bigger array of specimens [11].

The scanning electron microscope has a lot of advantages as compared to the traditional microscopes. Not only has it allowed more of a specimen to be in focus at one time, it also has much higher resolution that makes specimens capable to be magnified at much higher levels. Since SEM utilizes electromagnets rather than lenses, the researchers and scientists are more in control of the extent of magnification [11].

To use SEM, the specimens must first be made electrically conductive. This can be achieved by coating the samples with conductive materials such as thin layer of gold, platinum, palladium alloy, and so on [12]. This is normally done by using a device called a “sputter coater”. The sputter coater uses an electric field and argon gas. The sample is first placed in a vacuum condition of a small chamber. Argon gas and an electric field will then remove the electrons from the argon, which makes the atoms positively charged as the result. The argon ions will be attracted to a negatively charged gold foil. These argon ions attack the gold atoms at the surface of the gold foil, making these gold atoms fall and resolve on the surface of the sample, producing a thin gold coating as the result [11].

Comment: An SEM testing could be done to observe the surface morphology of the epoxy coating. Comparison would be made on the surface morphology of the epoxy coating before and after its exposure to the ionic liquids.

2.5 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR stands for Fourier Transform Infrared. It is the preferred technique of infrared spectroscopy whereby an infrared radiation is passed through a sample. By doing so, some of the infrared radiation is absorbed by the sample while some of it is transmitted. The result of the spectrum shows the molecular absorption and transmission, thus creating a molecular fingerprint of the sample. Similar to a fingerprint, the infrared spectrum is unique for each molecular structure. Due to this, infrared spectroscopy is applicable for several types of analysis [13]. FTIR can be used to:

- identify unknown materials
- determine the quality or consistency of a sample
- determine the amount of components in a mixture

An infrared spectrum signifies a fingerprint of a sample with absorption peaks which correspond to the frequencies of vibrations between the bonds of the atoms in the material. There will be no compound producing the same infrared spectrum because each different material is a unique combination of atoms. Therefore, it is certain that infrared spectroscopy would result in a positive identification for every kind of material. In addition to that, the size of the peaks in the spectrum indicates the amount of material present. Infrared is an excellent tool for quantitative analysis with the help of modern software algorithms. This results in a spectrum which is a plot of intensity vs. frequency. [13]

Comment: FTIR testing could be conducted to note the changes in spectroscopy of the epoxy coating if there is any. Similar to SEM testing, the comparison of the epoxy coating spectroscopy will be made before and after its exposure to the ionic liquids.

2.6 Pull-Off Adhesion Testing

Pull-off adhesion testing is normally conducted to measure the force required to pull a certain diameter of coating away from its substrate [24]. The major components of a pull-off adhesion tester consist of a pressure source, a pressure gage and an actuator. During the operation, the flat face of a pull stub (dolly) is adhered to the coating which is going to be evaluated. The bonding adhesive is allowed to cure before a coupling connector from the actuator is attached to the dolly. Pressure is slowly increased to the actuator by activating the pressure source. The moment the pressure in the actuator grows larger than the bond strength between the coating and the substrate, separation between the paint and its substrate occurs and the actuator-dolly assembly lifts the coating from the substrate. The system pressure gauge will provide the maximum pressure reading at which the pull-off will occur. Shown below is the figure of cross-sectional view of an actuator [25].

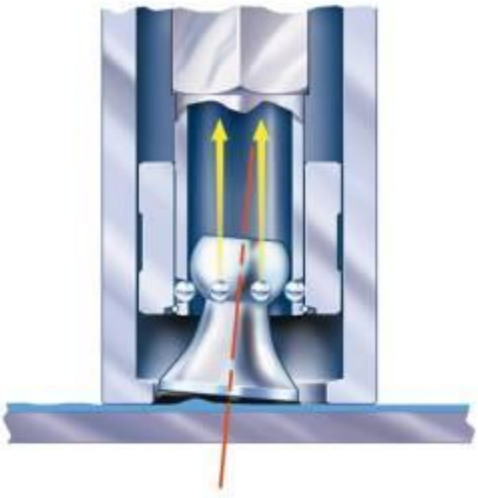


Figure 2.7: Cross-Sectional View of an Actuator [25]

Comment: Pull-off adhesion test would be an appropriate test to notice the changes in the bond strength of the epoxy before and after its exposure to ionic liquids if there is any. By doing this way, we would be able to identify if the exposure of ionic liquids to epoxy coating affect the bond strength of the epoxy or not.

2.7 Summary

The development of ionic liquids has been attracting a lot of attentions nowadays. It has vast potential to be applied in many industrial applications in the near future. On the other hand, epoxy coating has been applied extensively as protective material in storage tank and pipes. Epoxy is generally produced as a result of reaction between ‘resin’ and ‘hardener’. Despite its good protective properties, it was proven that long exposure to corrosive environment will reduce the coating protective properties. However, no research has been done yet to establish the effects or interaction between ionic liquids and epoxy coating. Since imidazolium based ionic liquids have shown big potential in desulphurization of fuels based on the researches done in the recent years, it will be selected for the experiment with epoxy coating.

One of the possible methods of experiment to be applied is the water absorption test. However, instead of being immersed in water, the samples of epoxy coating can be immersed in ionic liquids for a certain period of time and the weight increment is observed to calculate the percentage of ionic liquid uptake. Scanning Electron Microscope (SEM) and Fourier Transform Infrared (FTIR) interferometer can also be used to note the differences in surface morphology and material spectrum spectroscopy before and after the exposure of epoxy coating to ionic liquid. Pull-off adhesion testing should be conducted to note down the difference in bond strength of the polymer before and after its exposure to ionic liquids.

CHAPTER 3

METHODOLOGY

3.1 Research Methodology

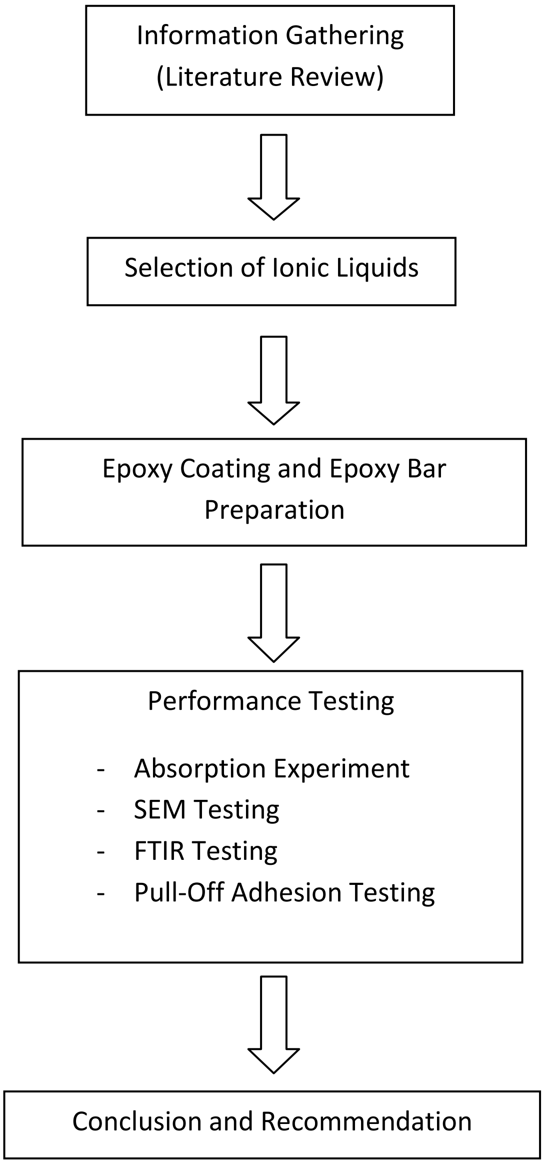


Figure 3.1 Project Process Flow

3.1.1 Selection of Ionic Liquids

The ionic liquids to be selected as specimens are as following:

1. 1-buthyl-3-methylimidazolium trifluoromethanesulfonate, [BMIM][OTF]
2. 1-ethyl-3- methylimidazolium diethyl phosphate, [EMIM][DEP]
3. 1-buthyl-3- methylimidazolium acetate[BMIM][AC]

3.1.2 Epoxy Coating Preparation

1. A carbon steel plate of 2mm thickness is prepared.
2. The specimens are cut to 40 mm x 40 mm for eight pieces.
3. The sample surface is then polished sequentially on 240, 320, 400, 600, 800 and 1200 grit SiC paper until previous rusts have been removed using grinder machine.

Figure 3.2: Grinder Machine

4. The specimens are degreased with acetone, rinsed in distilled water and then dried.
5. Unmodified diglycidyl ether of bisphenol A (DGEBA) and m-xylydiamine (m-XDA) are prepared.
6. DGEBA is put into a plastic container and the weight of DGEBA is measured.
7. m-XDA is added into the epoxy with ratio of 2:1. The required amount of DGEBA and m-XDA is calculated with equation as shown below:

$$M = \left[\frac{E}{E_{n_{epoxy}}}\right]\left[\frac{E_{n_{a\min e}}}{2}\right]$$

Equation 3.1

M is mass of m-XDA (g),

E is mass of DGEBA (g),

$E_{n_{epoxy}}$ is equivalent weight of DGEBA (g/mol), (390 g/mol)

$E_{n_{a\min e}}$ is equivalent weight of m-XDA (g/mol). (136 g/mol)

8. m-XDA is slowly added into DGEBA using pipette dropper until the calculated weight of m-XDA is achieved.
9. The mixture of m-XDA and DGEBA is stirred using a wood stick for roughly ten minutes.

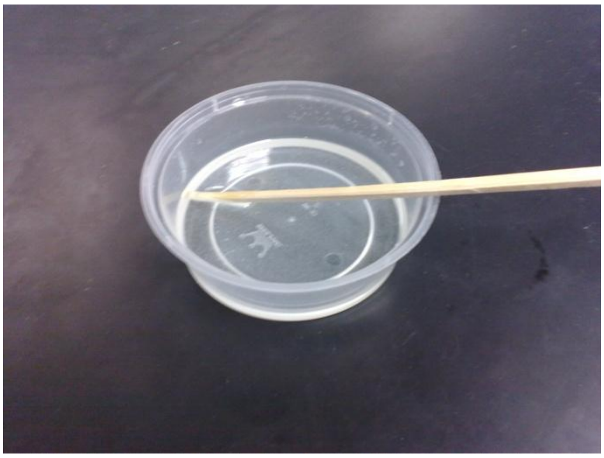


Figure 3.3: Mixture of DGEBA and m-XDA

10. The mixture is applied to the steel plate using a brush.
11. Four coatings are allowed to cure at room temperature for roughly 1 week while the other four coatings are fully cured at 60 ^{o}C for 1 hour before proceeding to 120 ^{o}C for 3 hours using oven.

3.1.3 Epoxy Bar Preparation

1. Unmodified diglycidyl ether of bisphenol A (DGEBA) and m-xylydiamine (m-XDA) are prepared.
2. DGEBA is put into a plastic container and the weight of DGEBA is measured.
3. The required amount of m-XDA is calculated using equation 3.1.
4. m-XDA is slowly added into DGEBA using pipette dropper until the calculated weight of m-XDA is achieved.
5. The mixture of m-XDA and DGEBA is stirred using a wood stick for roughly ten minutes.

6. The mixture of m-XDA and DGEBA is poured inside a mould as shown in Figure 3.3

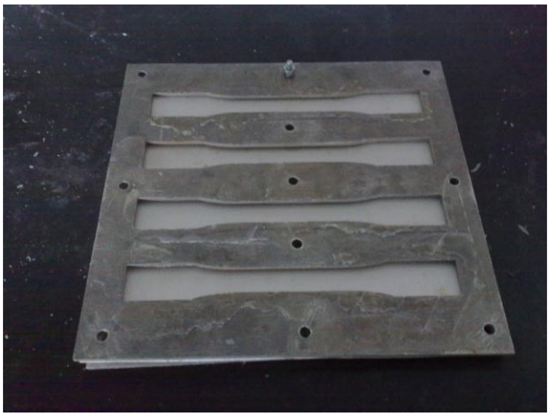


Figure 3.4: Mould Used to Prepare Epoxy Bar

7. The epoxy inside the mould is allowed to cure for 24 hours at room temperature.
8. The epoxy bar is taken out from the mould and cut into 4 small pieces of roughly 1cm x 2cm bars and allowed to cure further for 1 week at room temperature.
9. Step 1until 6 are repeated.
10. The mould is then put inside an oven and heated at 60 ^{o}C for 1 hour before proceeding to 120 ^{o}C for 3 hours.
11. The fully cured epoxy bar is taken out from the mould and cut into 4 small pieces of roughly 1cm x 2cm.

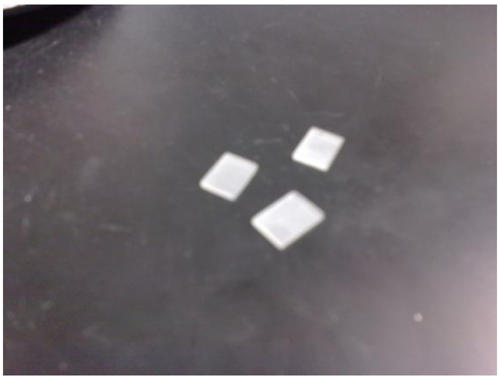


Figure 3.5: Epoxy Bars

3.1.4 Absorption Experiment

1. The initial weight of the epoxy bars (1cm x 2cm) are measured and recorded.
2. The water content of [BMIM][OTF], [EMIM][DEP], and [BMIM][AC] are measured and recorded using Karl Fischer Coulometer as shown in Figure 3.5.

Figure 3.6: Karl Fischer Coulometer

3. The epoxy coated plates and epoxy bars are then immersed in three different ionic liquids; [BMIM][OTF], [EMIM][DEP], and [BMIM][AC] as mentioned in step 2 using aluminium cup that are put inside an air tight container as shown in Figure 3.6.

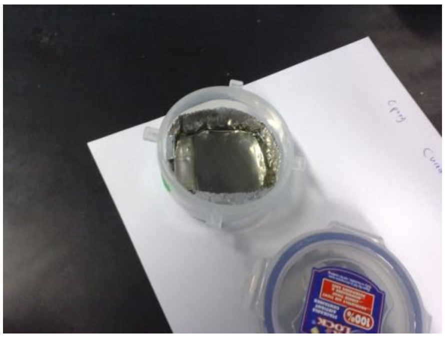


Figure 3.7: The Immersed Epoxy Coating and Epoxy Bar

4. The containers are put inside a glove box as shown in Figure 3.7.

Figure 3.8: Glove Box

5. Every 24 hours, the epoxy bar immersed in each ionic liquid will be weighed and recorded inside the glove box before it is immersed back in the respective ionic liquids.

   Note: The epoxy bar is first rinsed with acetone, cleaned with tissue paper and allowed to dry for 5 minutes before it is weighed.
6. Step 5 is repeated for 15 days.
7. Uptake percentage of ionic liquids for each day is calculated using equation 3.2 shown below.

$$\boxed{\%\ \text{Uptake} = \frac{\text{Weight after Immersion} - \text{Weight before Immersion}}{\text{Weight before Immersion}} \times 100}$$

Equation 3.2

3.1.5 Scanning Electron Microscope (SEM) Testing

1. The epoxy bars are coated with palladium alloy using sputter coater.

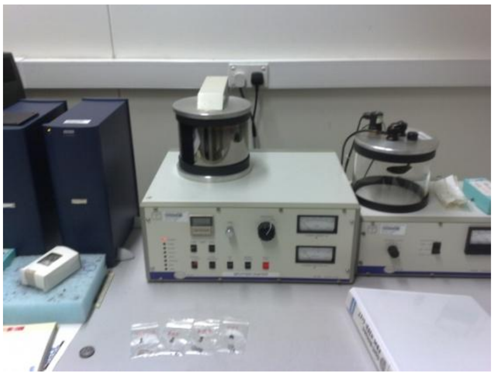


Figure 3.9: Sputter Coater

2. The samples are mounted firmly in the small chamber.
3. The samples are then placed in the SEM.
4. The surfaces are examined.

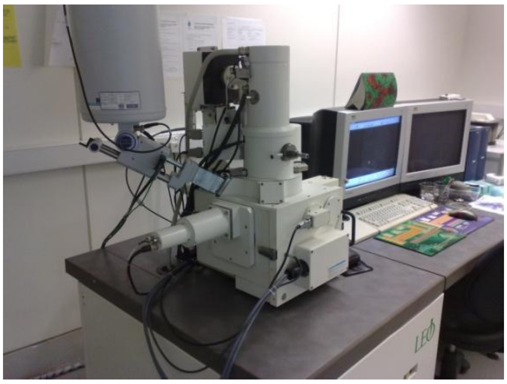


Figure 3.10: Scanning Electron Microscope

3.1.6 Fourier Transform Infrared (FTIR) Testing

1. Part of the epoxy bar is shredded to powder,
2. The epoxy powder is then mixed with potassium bromide powder, compressed with hand presser and placed on the sample holder.
3. Spectrometer operating software is then run.
4. The spectrum of the sample is recorded.
5. Step 1-4 are repeated for each sample of epoxy bar.

Figure 3.11: FTIR Spectrometer

3.1.7 Pull-Off Adhesion Testing

1. The surface of the dolly and the epoxy coated plate are de-greased by using acetone.
2. A small quantity of adhesive is mixed and applied on the prepared surface of the dolly.
3. The dolly is then placed on the test surface.
4. Pressure is applied to squeeze out any excessive adhesive and removed.
5. The adhesive is then allowed to cure.
6. The base support ring is placed on the dolly to ensure that it lies flat on the surface.
7. The handwheel or nut is slackened on the adhesion tester.
8. The dragging indicator is set to zero on the scale and the claw is engaged carefully with the dolly.

9. The adhesion tester is held steadily with one hand to prevent rotation.
10. The handwheel or nut is tightened slowly and evenly to apply an increasing force to the dolly, hence the coating.
11. Continue until the coating fails and dolly is removed from the surface. The pull-off force is read from the position of the dragging indicator after the test is completed.
12. Step 1-11 are repeated for each epoxy coated plate.

3.2 Project Activities

The project starts with information gathering pertaining to ionic liquids and epoxy coating. The activities that have been completed are as follows:

1) Submission of project proposal.
2) Grinding and polishing of carbon steel plates.
3) Preparation of epoxy coatings and epoxy bar.
4) Immersion of epoxy coatings and epoxy.
5) Absorption test, pull-off adhesion test, FTIR test, and SEM test.

3.3 Gantt Chart

Activity	W1	W2	W3	W4	W5	W6	W7	W8	W9	W10	W11	W12	W13	W14	W15
Grinding and Polishing of Carbon Steel Plates	▨	▨	▨												
Preparation of Epoxy Coating and Epoxy Bar				▨	▨	▨									
Immersion of Epoxy in Ionic Liquids							▨	▨							
Absorption Test							▨	▨							
FTIR Test									▨						
Pull Off Adhesion Test									▨						
SEM Test													▨		
Submission of Dissertation														▨	
Submission of Technical Paper															▨
Oral Presentation															▨

Figure 3.11: Project Gantt Chart

3.4 Tools Required

Scanning Electron Microscope (SEM), sputter coater, pull-off adhesion tester, Fourier Transform Infrared Spectroscopy (FTIR) interferometer, glove box, Karl Fischer coulometer, grinder machine, weight measurer, plastic container, and mould.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Absorption Test

The epoxy bars were immersed in three different ionic liquids which are [BMIM][OTF], [EMIM][DEP], and [BMIM][AC]. Before the experiment took place, the water content of the above ionic liquids were measured and recorded as shown in Table 4.1.

Ionic Liquids	Concentration (ppm)	Concentration (%)
[BMIM][OTF]	610	0.06
[EMIM][DEP]	14640	1.46
[BMIM][AC]	18770	1.88

Table 4.1: Water Content in Ionic Liquids

The percentage of ionic liquids uptake versus days graphs were plotted as shown below.

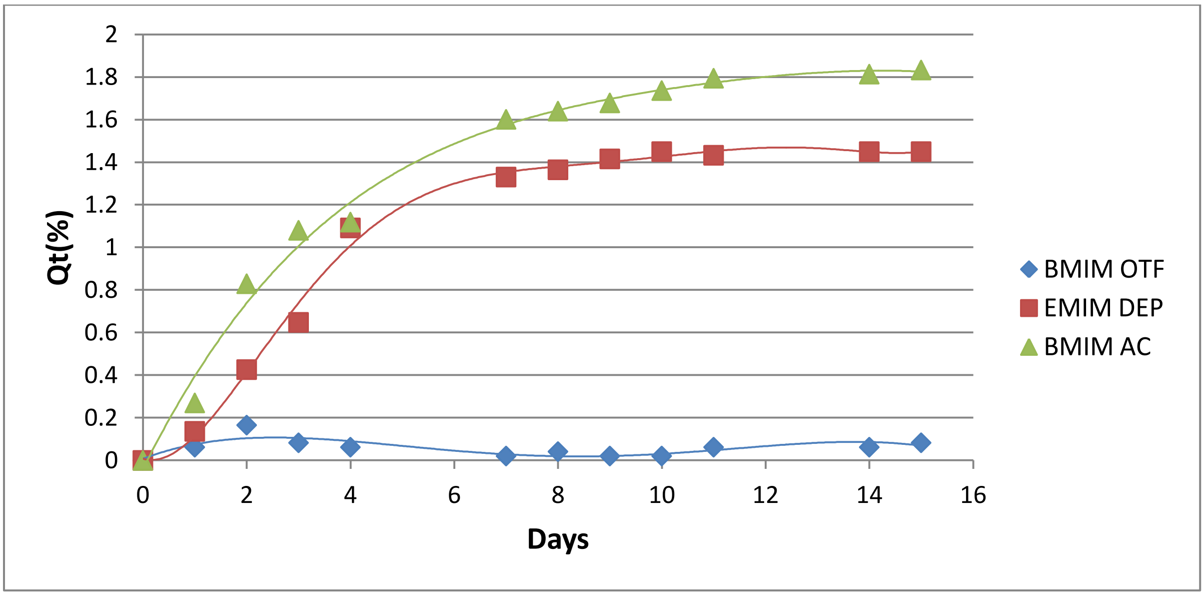


Figure 4.1: Percentage of Ionic Liquid Uptake, Qt (%) in Epoxy Cured at 25 ^{o}C

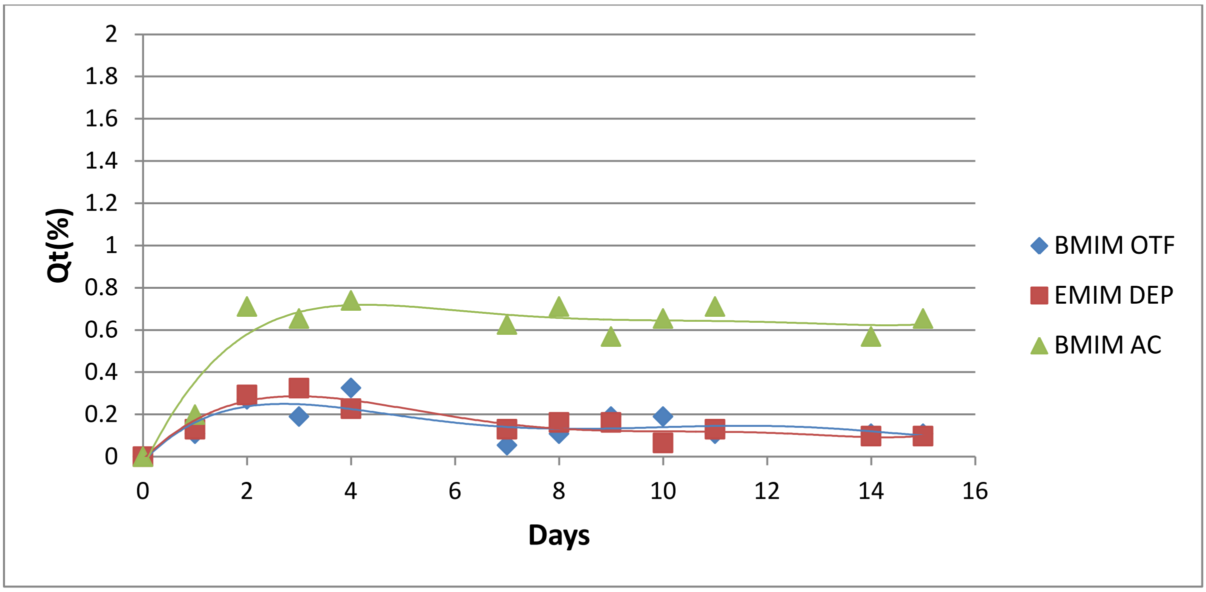


Figure 4.2: Percentage of Ionic Liquid Uptake, Qt (%) in Epoxy Cured at 120 ^{o}C

Based on the graphs shown above, different curing condition of the epoxy results in different trend of ionic liquids uptake. [BMIM][OTF] is noted to have a very minimum uptake percentage in both curing conditions of the epoxy. [BMIM][AC] on the other hand shows a big uptake percentage in both curing conditions of the epoxy, which is notably the highest compared to [BMIM][OTF] and [EMIM][DEP]. The uptake percentage of [EMIM][DEP] however varies in different curing condition of the epoxy. It is noted that [EMIM][DEP] has high uptake percentage in epoxy cured at room temperature although slightly lower compared to [BMIM][AC]. However, [EMIM][DEP] has lower uptake percentage in epoxy cured at 120 ^{o}C compared to epoxy cured at room temperature, 25 ^{o}C.

Molecular weight of [BMIM][OTF], [EMIM][DEP] and [BMIM][AC] are 288 g/mol, 264 g/mol, and 198 g/mol respectively. High uptake percentage of [BMIM][AC] in epoxy is probably because of its relatively small size compared to [BMIM][OTF] and [EMIM][DEP] making it easier to penetrate the epoxy. The difference in uptake percentage of [EMIM][DEP] in epoxy cured at room temperature and 120 ^{o}C might be explained by the nature of the epoxy polymer itself. Epoxy that is cured at 120 ^{o}C is fully cured, thus have cross-linked more compared to epoxy cured at room temperature which makes it harder to penetrate.

4.2 Pull-Off Adhesion Test

Epoxy Coating

Thickness: 0.3mm

Temperature of Immersion: 25 °C (Room Temperature)

Curing Temperature of Epoxy (°C)	Pull-Off Force (MPa)			
	Before Immersion in Ionic Liquids	After Immersion in Ionic Liquids		
		BMIM OTF	BMIM AC	EMIM DEP
25	3	3	2	2.5
120	3	3	2.5	3

Table 4.2: Result of Pull-Off Adhesion Test

[BMIM][OTF] does not seem to be affecting the adhesion strength of epoxy coating. [BMIM][AC] on the other hand has shown to have affected the adhesion strength of epoxy coating after 15 days of immersion. It reduces the adhesion strength of epoxy coating cured at 25 °C by 33.33% and 16.67% for epoxy coating cured at 120°C. [EMIM][DEP] does not affect the adhesion strength of epoxy cured at 120°C, but it reduces the adhesion strength of epoxy cured at 25 °C slightly by 16.67%.

4.3 Fourier Transform Infrared (FTIR) Test

NOTE: Refer to Appendix for Clearer Results of FTIR

Epoxy Cured at 25 ^{o}C:

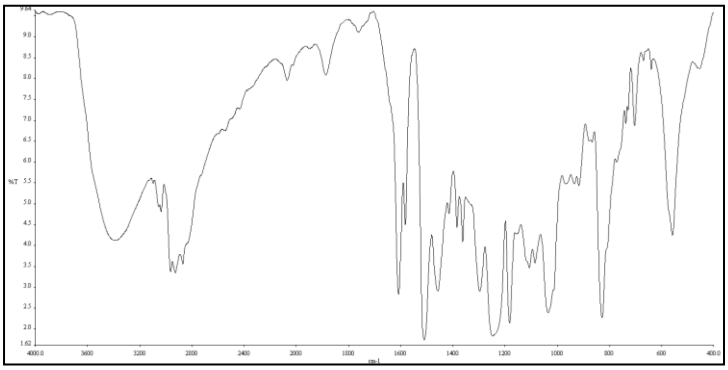


Figure 4.3: Infrared Spectroscopy of Epoxy (Cured at 25 ^{o}C) before Immersion

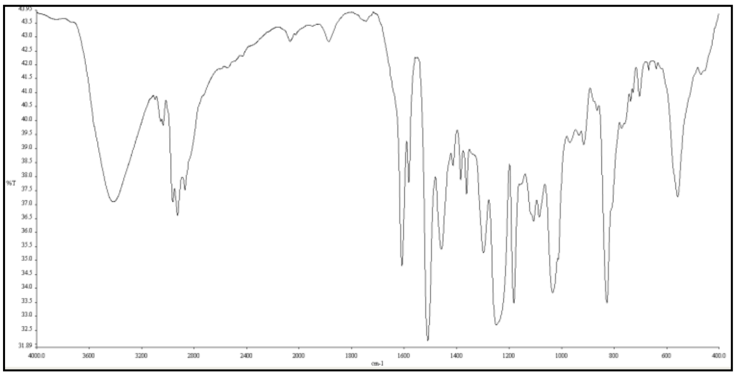


Figure 4.4: Infrared Spectroscopy of Epoxy (Cured at 25 ^{o}C) after Immersion in [BMIM][AC]

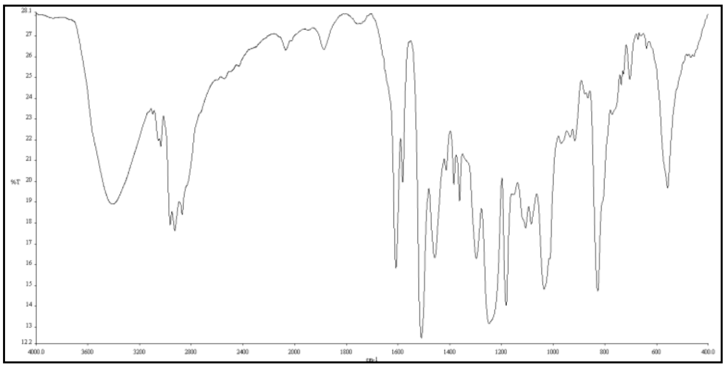


Figure 4.5: Infrared Spectroscopy of Epoxy (Cured at 25 ^{o}C) after Immersion in [BMIM][OTF]

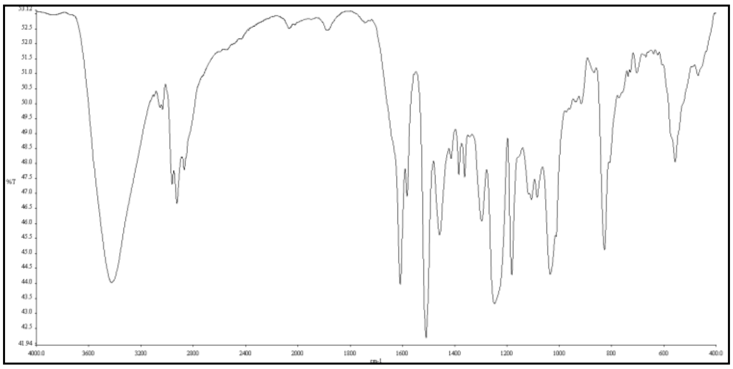


Figure 4.6: Infrared Spectroscopy of Epoxy (Cured at 25 ^{o}C) after Immersion in [EMIM][DEP]

Epoxy Cured at 120 ^{o}C:

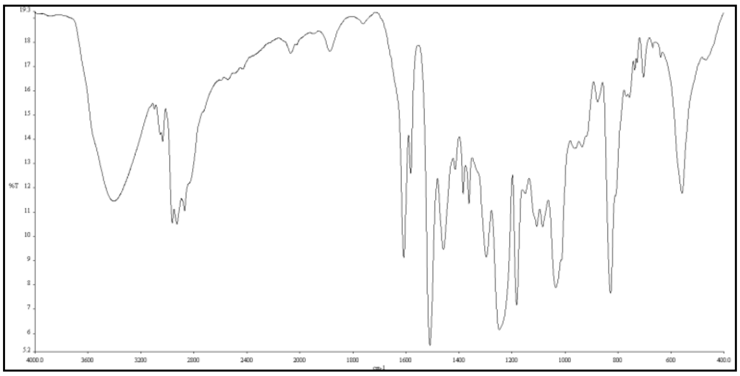


Figure 4.7: Infrared Spectroscopy of Epoxy (Cured at 120 ^{o}C) before Immersion

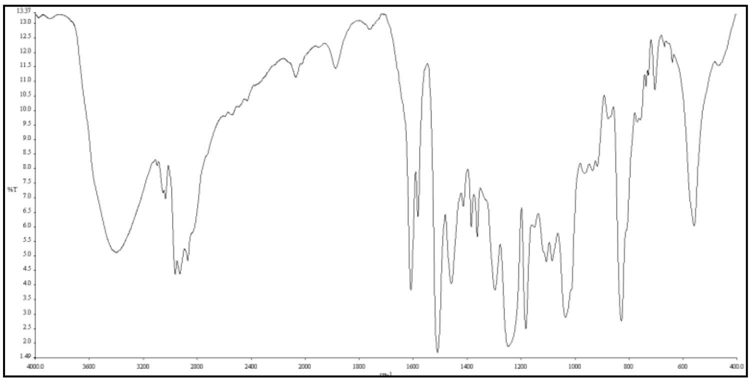


Figure 4.8: Infrared Spectroscopy of Epoxy (Cured at 120 ^{o}C) after Immersion in [BMIM][AC]

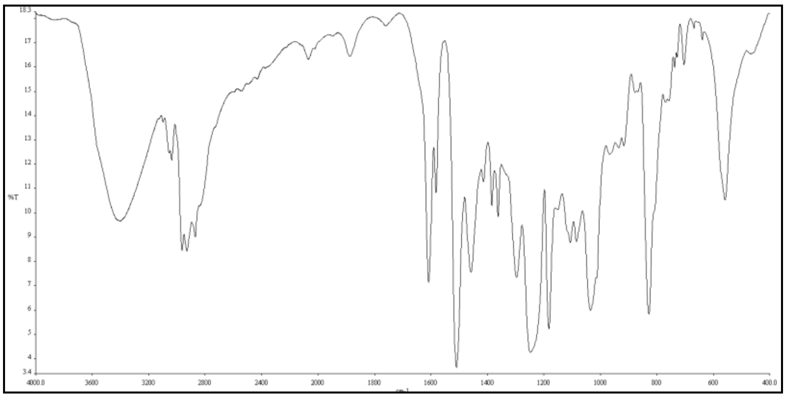


Figure 4.9: Infrared Spectroscopy of Epoxy (Cured at 120 ^{o}C) after Immersion in [BMIM][OTF]

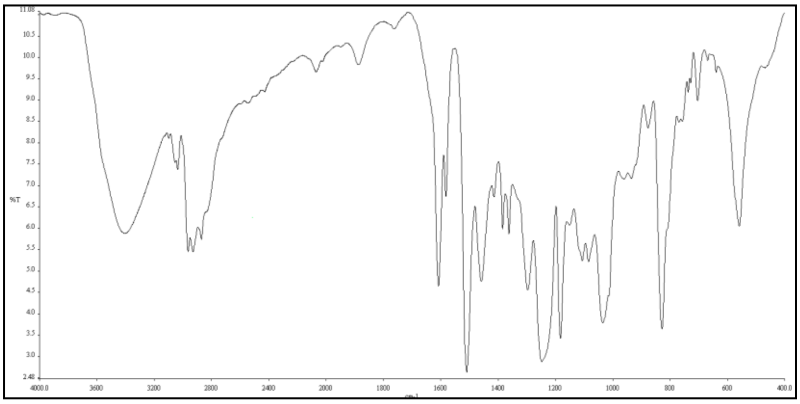


Figure 4.10: Infrared Spectroscopy of Epoxy (Cured at 120 ^{o}C) after Immersion in [EMIM][DEP]

Comparing all infrared spectroscopy of the samples, it is noted that there is no significant difference in the trend of the peaks. Therefore, it is safe to say that the material composition of the epoxy does not change after immersion in the ionic liquids.

4.4 Microscope Images

<u>Optical Microscope (30x Magnification):</u>

Epoxy Cured at 25 ^{o}C:

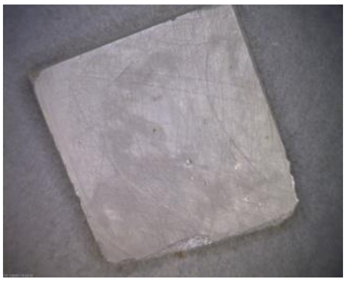
Blank (Before Immersion) 	After Immersion in [BMIM][AC] 
After Immersion in [BMIM][OTF] 	After Immersion in [EMIM][DEP] 

Figure 4.11: Images of Epoxy Bar (Cured at 25 ^{o}C) – 30x Magnification

Epoxy Cured at 120 ^{o}C:

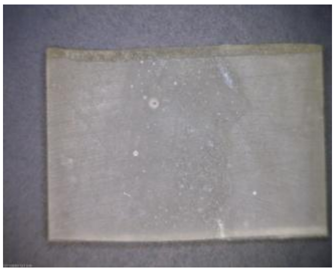
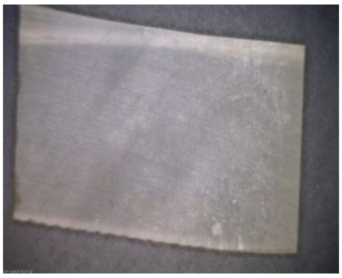
Blank (Before Immersion) 	After Immersion in [BMIM][AC] 
After Immersion in [BMIM][OTF] 	After Immersion in [EMIM][DEP] 

Figure 4.12: Images of Epoxy Bar (Cured at 120 ^{o}C) – 30x Magnification

Optical Microscope (60x Magnification):

Epoxy Cured at 25 ^{o}C:

Blank (Before Immersion) 	After Immersion in [BMIM][AC] 
After Immersion in [BMIM][OTF] 	After Immersion in [EMIM][DEP] 

Figure 4.13: Images of Epoxy Bar (Cured at 25 ^{o}C) – 60x Magnification

Epoxy Cured at 120 ^{o}C:

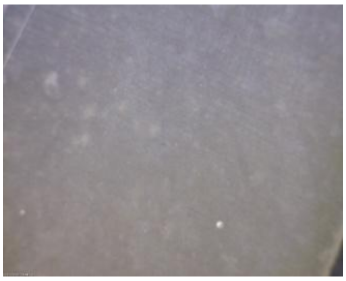
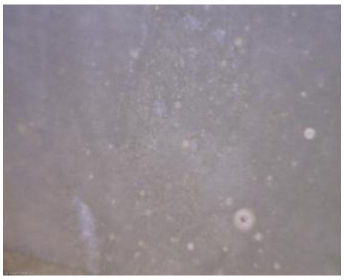
Blank (Before Immersion) 	After Immersion in [BMIM][AC] 
After Immersion in [BMIM][OTF] 	After Immersion in [EMIM][DEP] 

Figure 4.14: Images of Epoxy Bar (Cured at 120 ^{o}C) – 60x Magnification

Scanning Electron Microscope (1000x Magnification)

Epoxy cured at 25 ^{o}C:

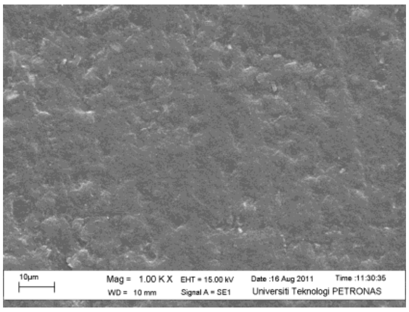
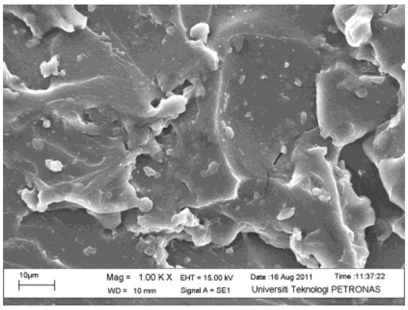
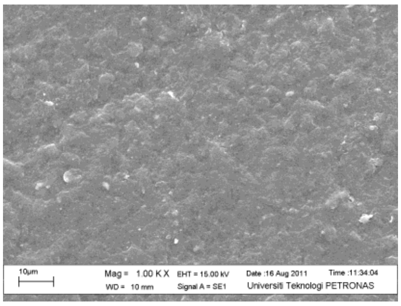
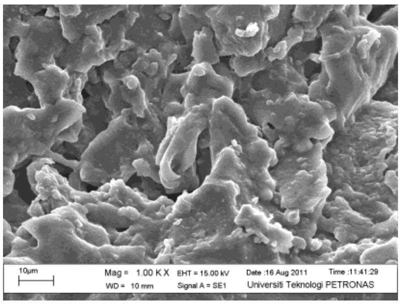
Blank (Before Immersion) 	After Immersion in [BMIM][AC] 
After Immersion in [BMIM][OTF] 	After Immersion in [EMIM][DEP] 

Figure 4.15: Images of Epoxy Bar (Cured at 25 ^{o}C) – 1000x Magnification

Epoxy cured at 25 ^{o}C appears to be more vulnerable to the attack of ionic liquids compared to epoxy that is fully cured at 120 ^{o}C. From the microscope images of the samples, unknown white substance appears on the surface of epoxy bars that is cured at 25 ^{o}C after being immersed in [BMIM][AC] and [EMIM][DEP]. The SEM images of epoxy cured at 25 ^{o}C also show rough surface morphology after being immersed in [BMIM][AC] and [EMIM][DEP] which indicate some attacks of the ionic liquids. Clear image is obtained for epoxy that is immersed in [BMIM][OTF] which means there is no attack on the surface of the epoxy by [BMIM][OTF].

4.5 Discussion

Based on the absorption graph, absorption rate of ionic liquids in epoxy are dependent on curing condition of the epoxy and the type of ionic liquids used. Of all the ionic liquids; [BMIM][AC],[BMIM][OTF], and [EMIM][DEP], [BMIM][AC] has the smallest molecular weight, followed by [EMIM][DEP] and lastly [BMIM][OTF]. It is logical that [BMIM][AC] exhibits high absorption rate in epoxy because of its relatively small size compared to [EMIM][DEP] and [BMIM][OTF]. Furthermore, fully cured epoxy shows greater resistance to absorption of ionic liquids compared to partially cured epoxy. This is explained by the nature of the epoxy polymer itself. Epoxy that is fully cured have cross-linked more compared to partially cured epoxy which makes it harder to penetrate.

The microscope images prove that [BMIM][AC] and [EMIM][DEP] attack the surface of partially cured epoxy. The unknown white substance on the surface of epoxy might be the result of the attacks.

Even so, material composition of the epoxy does not change despite having shown some corrosion on the surface of partially cured epoxy after being immersed in [BMIM][AC] and [EMIM][DEP]. This is verified by the FTIR results.

From the pull-off adhesion test results, it is noted that some ionic liquids reduce the adhesion strength of epoxy coating depending on curing condition of the epoxy as well. Fully cured epoxy shows greater resistance to the attack of ionic liquids such as [BMIM][AC] and [EMIM][DEP]. However, it is also discovered that some ionic liquids such as [BMIM][OTF] has no significant impact on epoxy which makes it suitable to be commercialized fully in the future. Loss of adhesion will create a lot of problems in the industry. Therefore, careful screening of ionic liquids must be done before it is stored in storage tanks or transported via pipes that have epoxy paint.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusion

1. Absorption rate of ionic liquids in epoxy is dependent on the type of ionic liquids used. Ionic liquids of small molecular size tend to have high absorption rate compared to bigger molecular size ionic liquids.
2. Absorption rate of ionic liquids in fully cured epoxy is lower compared to epoxy that is partially cured.
3. Fully cured epoxy shows greater resistance to ionic liquids attack compared to partially cured epoxy.
4. [BMIM][AC] and [EMIM][DEP] indicate some attacks on the surface of epoxy.[BMIM][OTF] on the other hand does not show any significant impact on the epoxy. Therefore, all ionic liquids must undergo careful screening process before it is stored in storage tanks or transported via pipes that apply epoxy coating.

5.2 Recommendation

1. Immerse the epoxy in wider range of ionic liquids.
2. Increase the duration of immersion.
3. Repeat the experiment at least once to get better accuracy of results.

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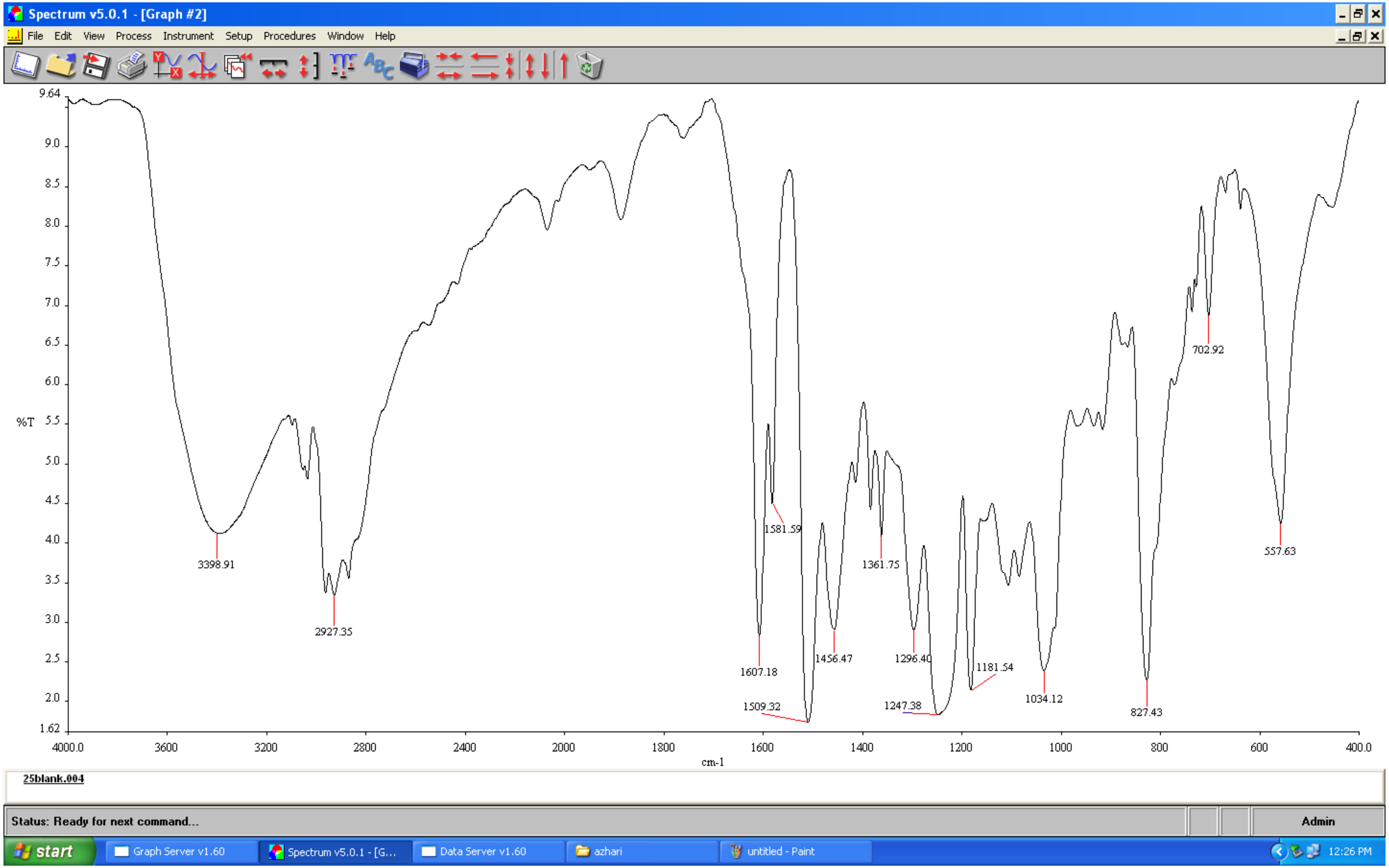
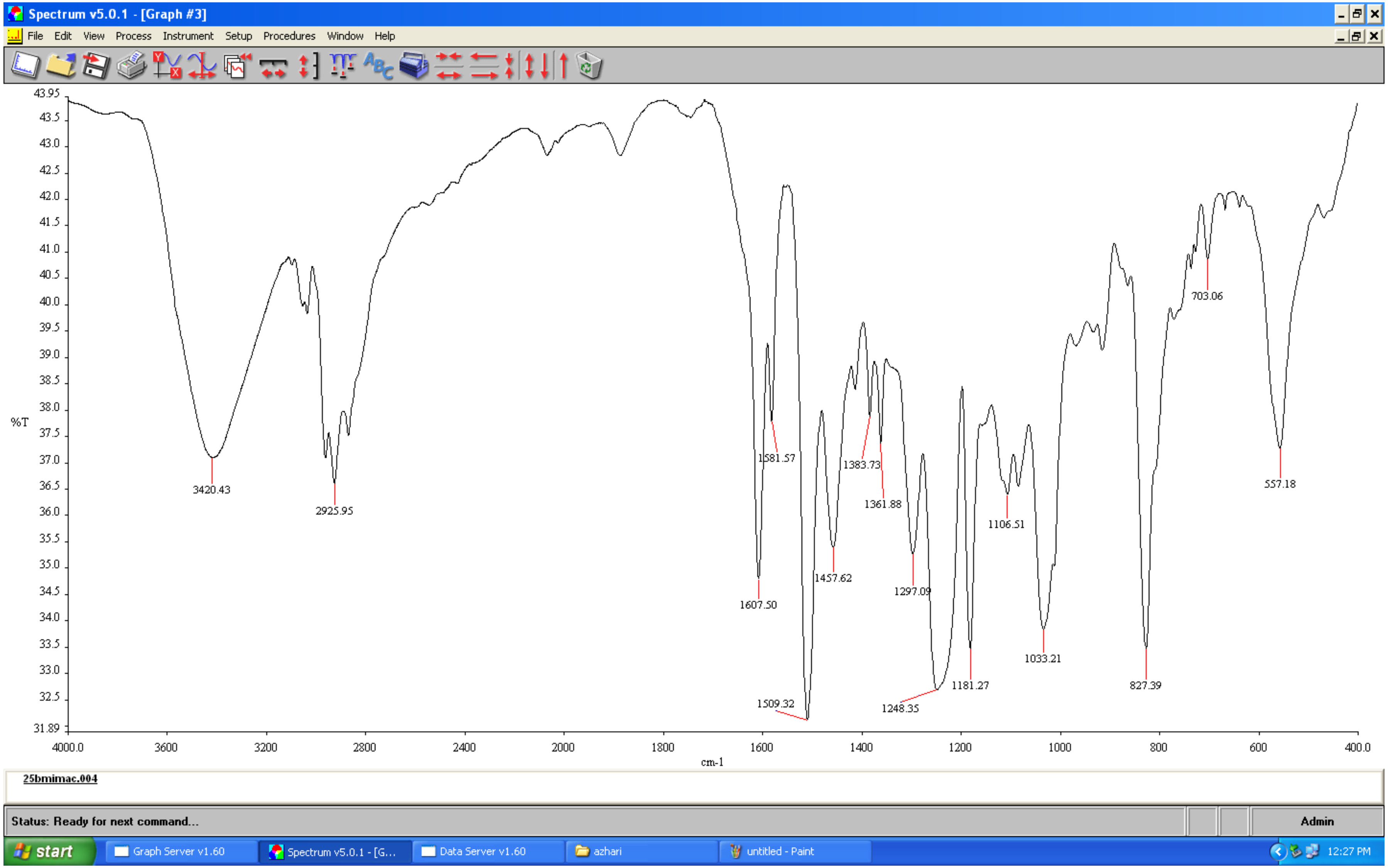
APPENDICES

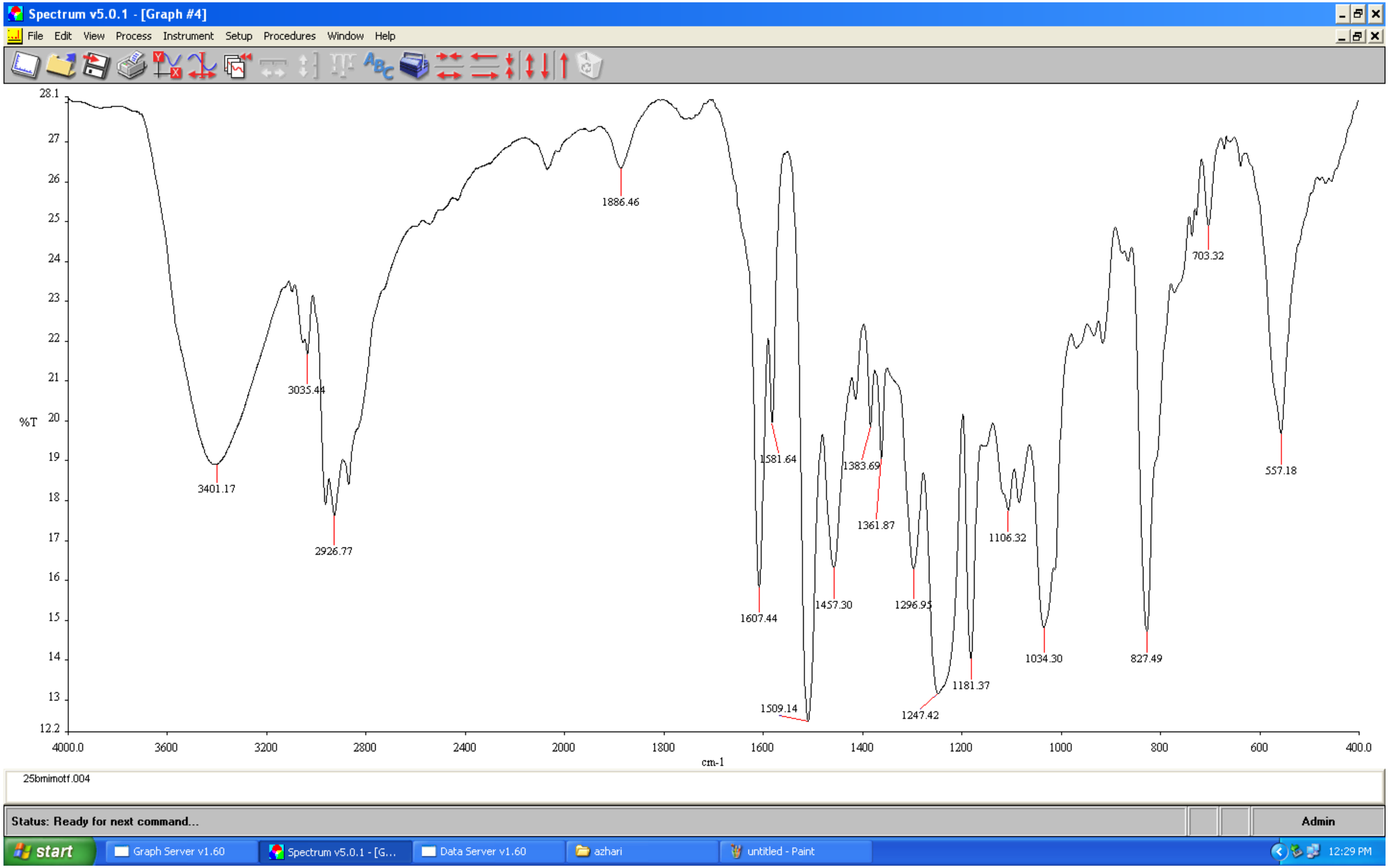


Infrared Spectroscopy for Epoxy Cured at 25 °C (Before Immersion)



Status: Ready for next command...

Infrared Spectroscopy for Epoxy Cured at 25 ^{o}C (Immersed in [BMIM][AC])



25bmimotf.004

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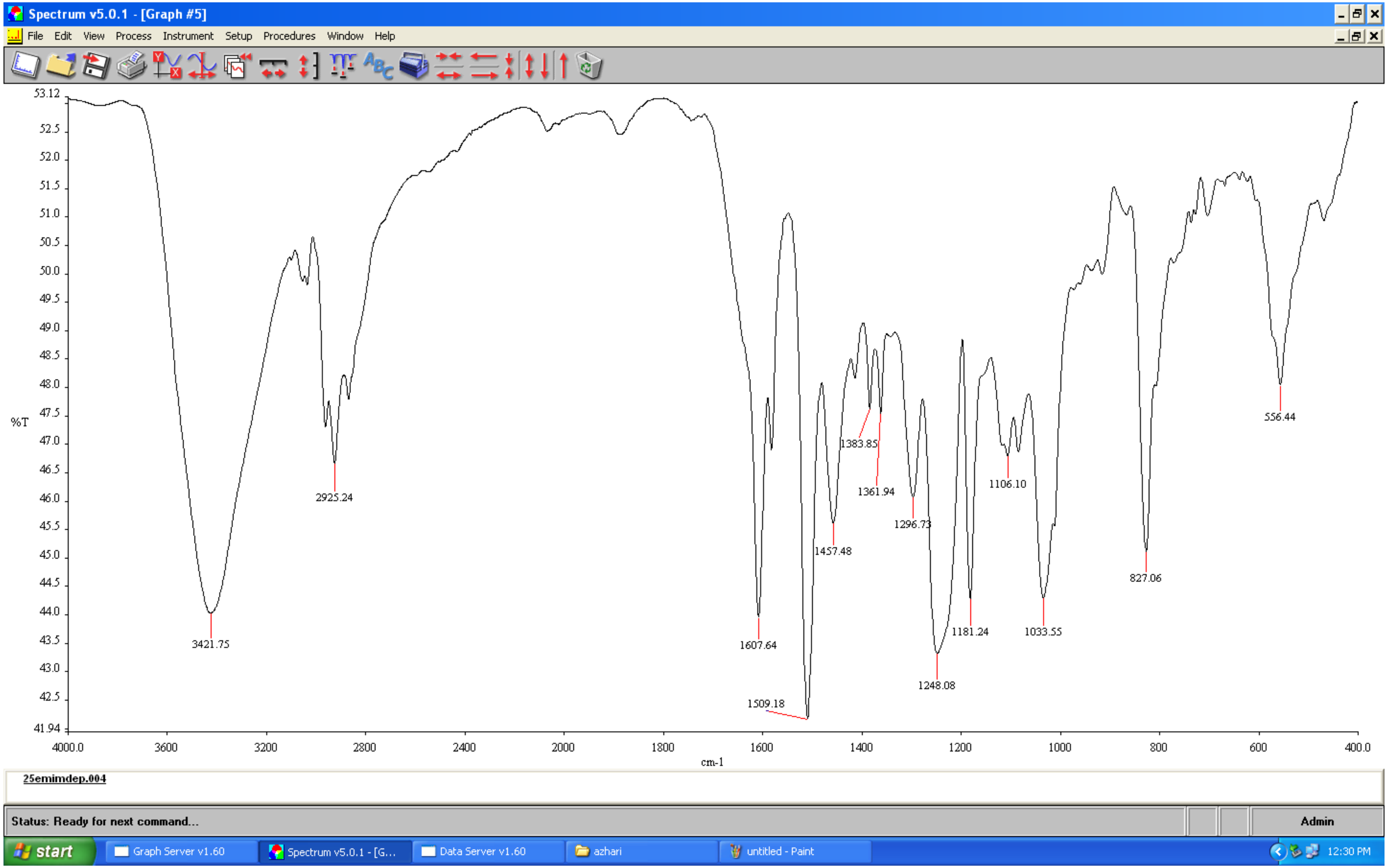

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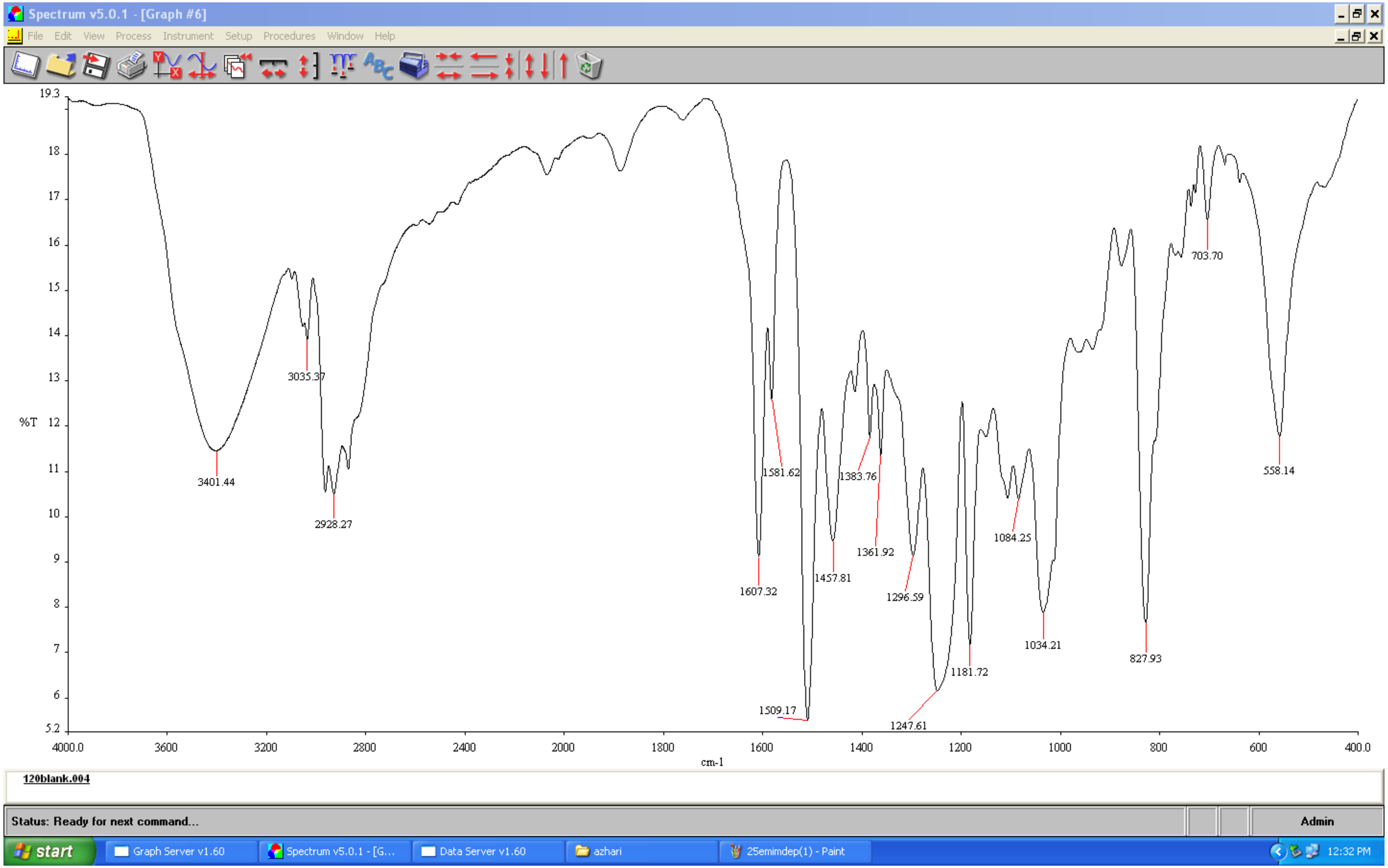

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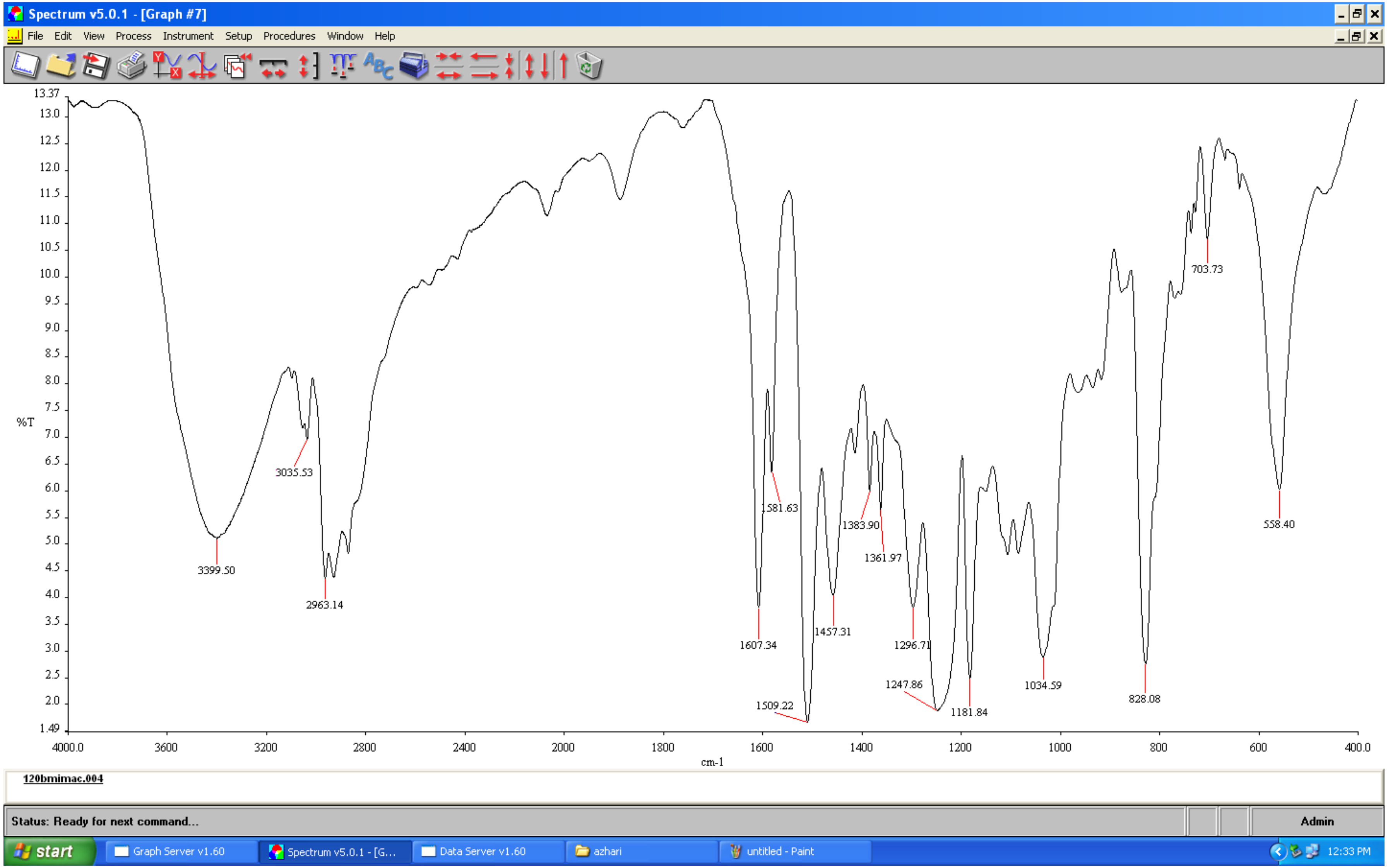
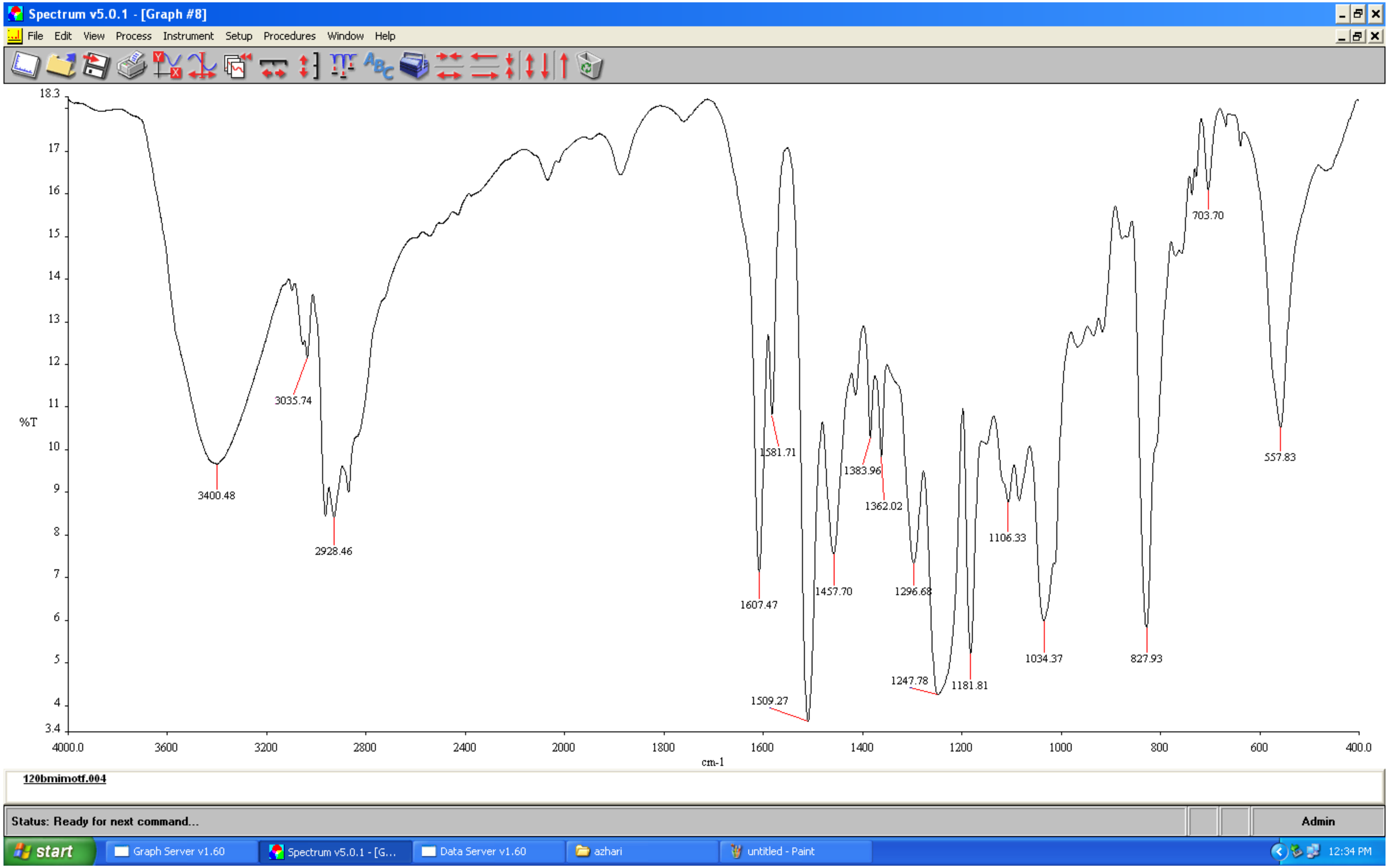
Infrared Spectroscopy for Epoxy Cured at 120 °C (Before Immersion)



120bmimac.004

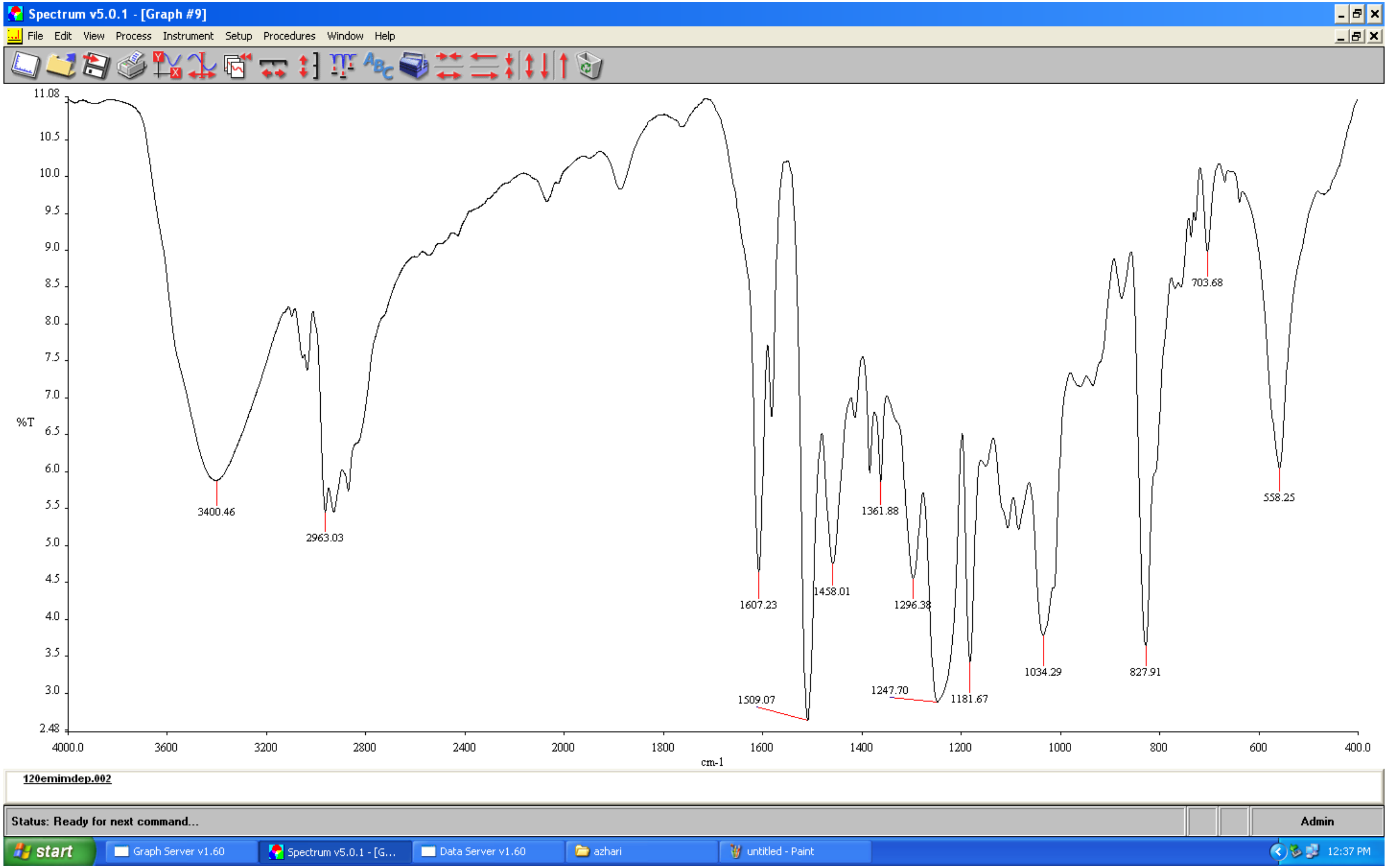
Status: Ready for next command...

Infrared Spectroscopy for Epoxy Cured at 120 °C (Immersed in [BMIM][AC])



Status: Ready for next command...

Infrared Spectroscopy for Epoxy Cured at 120 ^{o}C (Immersed in [BMIM][OTF])



120emimdep.002

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