DETERMINATION OF GEL CONTENT BY INCORPORATING IMIDAZOLIUM BASED IONIC LIQUID AS A CO-SOLVENT FOR EPOXIDIZED NATURAL RUBBER (ENR)

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ABSTRACT

Epoxidized natural rubber (ENR) exhibits high gel properties where the sample preparation part is being restricted by the use of suitable solvent for dissolution process prior to the instrumental analysis. Two types of ENR (ENR 25 and ENR 50) were dissolved in organic solvent with the addition of ionic liquid (IL) that acts as a co-solvent. Two types of imidazolium based ILs namely 1-butyl-3-methylimidazolium chloride (BmimCl) and 1-ethyl-3-methylimidazolium acetate **(**EmimAc) were used in this study**.** The changes in gel composition in ENR with the incorporation of IL were monitored through gel content analysis. ENR 25 and ENR 50 were soaked in different solvents have demonstrated quite similar mean percentage of macro gel that ranging from 42.07 % to 45.19 %. The increasing values of macro gel were observed for ENR 25 dissolved in THF and BmimCl (ENR 25+THF+BmimCl) as compared to ENR 25 dissolved in THF (ENR 25+THF). There are no significant changes of the macro gel values of ENR 50+THF+BmimCl to compare with ENR 50+THF. Both ENR 25 and ENR 50 which were dissolved in THF+EmimAc have showed lower macro gel values after the third leaching cycle. The macro gel value with large standard deviation between replication was obtained for ENR 50+THF+EmimAc due to inefficient leaching process. It was observed that the incorporation of BmimCl and EmimAc during gel content determination was unable to reduce the gel content in ENR, however species other than epoxide such as trans-diol and furan were found.

ABSTRAK

Getah asli terepoksida (ENR) mempunyai kandungan gel yang tinggi menyebabkan proses penyediaan sampel agak sukar dari segi penggunaan pelarut yang sesuai untuk melarutkan sampel sebelum dapat dianalisis menggunakan instrumen. Dua jenis gred ENR (ENR 25 dan ENR 50) telah dilarutkan di dalam pelarut organik dengan penambahan cecair ionik (IL) untuk membantu di dalam proses pelarutan. Dua jenis IL berdasarkan kumpulan imidazolium iaitu 1-butil-3-metilimidazolium klorida (BmimCl) dan 1-etil-3-metilimidazolium asetat (EmimAc) telah digunakan di dalam kajian ini. Perubahan dalam komposisi gel ENR dengan penambahan IL dipantau melalui analisis kandungan gel. ENR 25 dan ENR 50 yang telah direndam di dalam tiga jenis pelarut organik yang berbeza menunjukkan purata peratusan makro gel di dalam julat 42.07 % - 45.19 %. Terdapat peningkatan nilai makro gel bagi ENR 25 yang dilarutkan di dalam THF dan BmimCl (ENR 25+THF+BmimCl) berbanding ENR 25 yang dilarutkan di dalam THF (ENR 25+THF). Tiada perubahan ketara untuk nilai makro gel bagi ENR 50+THF+BmimCl jika dibandingkan dengan ENR 50+THF. Kedua-dua ENR 25 dan ENR 50 yang dilarutkan di dalam THF+EmimAc menunjukkan nilai makro gel yang lebih rendah selepas melalui proses larut lesap pada kitaran yang ketiga. Nilai makro gel dengan sisihan piawai yang tinggi di antara replikasi telah diperolehi bagi ENR 50+THF+EmimAc disebabkan oleh proses larut lesap yang tidak cekap. Diperhatikan bahawa penambahan BmimCl dan EmimAc semasa penentuan kandungan gel tidak berupaya mengurangkan kandungan gel di dalam ENR, walaubagaimanapun kehadiran spesies lain selain daripada epoksida seperti trans-diol dan furan telah dikesan.

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LIST OF SYMBOLS AND ABBREVIATIONS

AmimCl	**1- ALLYL-3 ACETIC ACID METHYL IMIDAZOLE**
BmimCl	**1-BUTYL-3-METHYLIMIDAZOLIUM CHLORIDE**
COSY	**HOMONUCLEAR CORRELATION SPECTROSCOPY**
DSC	**DIFFERENTIAL SCANNING CALORIMETER**
E%	**PERCENTAGE OF EPOXIDATION**
EmimAc	**1-ETHYL-3-METHYLIMIDAZOLIUM ACETATE**
ENR	**EPOXIDIZED NATURAL RUBBER**
FTIR	**FOURIER TRANSFORM INFRARED**
GPC	**GEL PERMEATION CHROMATOGRAPHY**
HETCOR	**HETERONUCLEAR CORRELATION SPECTROSCOPY**
HMBC	**HETERONUCLEAR MULTIPLE-BOND CORRELATION SPECTROSCOPY**
IL	**IONIC LIQUID**
MRB	**MALAYSIAN RUBBER BOARD**
NMR	**NUCLEAR MAGNETIC RESONANCE**
NR	**NATURAL RUBBER**

RO%	**PERCENTAGE OF RING OPENING**
RRIM	**RUBBER RESEARCH INSTITUTE OF MALAYSIA**
SMR CV	**STANDARD MALAYSIAN RUBBER CONSTANT VISCOSITY**
THF	**TETRAHYDROFURAN**

CHAPTER 1: INTRODUCTION

Epoxidized natural rubber (ENR) is one of the modified rubbers from natural rubber (NR). The modification process was done by introducing oxygen atom to the unsaturated molecule of NR which is well known to react very readily with peracids[1]. This chemical reaction will produce oxirane or epoxide compound that consists of three-membered ether in a cyclic form. ENR exhibit three-membered ring which is highly strained and therefore, it is reactive towards nucleophilic substitution. The epoxides can undergo acid-catalysed or base-catalysed ring opening reactions to form undesirable secondary products[2].

Formic acid and hydrogen peroxide were used in the current process for production of ENR[3]. Under carefully controlled conditions, NR latex can be epoxidised to over 75 mole % by minimizing the formation of secondary ring opening structure. Secondary reactions must be minimized for the production of ENR which exhibit good vulcanisate properties and processing behaviour acceptable in factory operations. A systematic study of the epoxidation of NR latex revealed that high total acid concentrations and elevated temperatures favoured the formation of secondary ring opening products[4].

Epoxidation products which attributed to the crosslinking reaction that cause gel formation are generally insoluble[5]. A study to investigate and determine the correlation between secondary ring openings for each grade of ENR has been done and was found that with the increase in percentage of acid brought about an increase in the Mooney viscosity and gel content values[6]. This modification transfers slightly polar natural rubber to highly polar rubber[7]. The properties are also changed due to the polarity changed. The polarity of ENR increases with rise in epoxide content. As the polarity in the chain molecules increases, the resistance to hydrocarbon oils, solvents, greases, etc. also increases. At high epoxidation levels e.g. ENR 50 these materials become more resistant to hydrocarbons but their resistance to polar solvents decreases[5].

Chemicals characterization of the raw ENR is very important to determine the properties of the rubber. Some of the properties measured are percentage of epoxidation level and molecular weight of the raw ENR. Due to high gel properties exhibit by ENR, the sample preparation part is being restricted by the use of suitable solvent for dissolution process prior to instrumental analysis. Currently, epoxidation level of various grades of ENR is determined by using ^{1}H NMR technique. Gel was formed after being soaked overnight with deuterated solvent which indicate incomplete dissolution of the raw ENR, hence only the solution part is being analysed. Eventhough the epoxidation level values were successfully determined, the ability to dissolve ENR completely prior to NMR determination may give additional information from the spectrum obtained. The other problem related to incomplete dissolution arises when analysing the raw ENR using gel permeation chromatography (GPC) for the determination of molecular weight. The ENR is not dissolved completely using the selected solvent due to gel formation. A study has proven that ENR were thoroughly soluble in toluene, tetrahydrofuran (THF) and chloroform after depolymerisation[8].

Since ENR is partially soluble in limited organic solvents, indigenous method using appropriate solvent need to be developed for complete dissolution of ENR for the chemicals characterization analysis. It is the intention of this study to include ionic liquids (ILs) as a co-solvent in order to help in the dissolution process of ENR that exhibit high gel properties. ILs are complex and versatile solvents capable to interact via hydrogen bonding, $\Pi - \Pi$, $n - \Pi$, dispersive, dipolar, electrostatic and hydrophobic interactions. IL has high ionic character that enhances the reaction rates to a great extent in many reactions including microwave-assisted organic synthesis as well as polymerization reactions. Solubility of ILs depends upon the nature of the cations and counter anions[9]. The use of ILs in ENR application has revolved around polymer electrolyte system in enhancing ionic conductivity[10,11]. However, there is no study on the dissolution of the gel part of ENR using IL has been investigated. Hence, the investigation on the suitability of IL for dissolving the gel part of ENR was done by similar approach, which was demonstrated in the dissolution study of cellulose using same group of IL. It is well known fact that ILs which consist of a number of cations and many different anions, are able to dissolve cellulose as direct solvents[12]. However, by considering the relative high cost of the ILs themselves, it is wise to use IL as a co-solvent in the dissolution process.

The purpose of the present study is to investigate and evaluate the solubility of two types of ENR (ENR 25 and ENR 50) in selected organic solvent with the addition of IL that acts as a co-solvent. Two types of imidazolium based ILs namely 1-butyl-3-methylimidazolium chloride (BmimCl) and 1-ethyl-3-methylimidazolium acetate (EmimAc) will be used in this study. The changes in gel composition in ENR with the incorporation of IL will be monitored through gel content analysis. The characterization of various gel and solution from this study will be done using Fourier Transform Infrared (FTIR), Nuclear Magnetic Resonance (NMR) and Differential Scanning Calorimeter (DSC) for identification of any chemical changes with regards to the dissolution process.

CHAPTER 2: LITERATURE REVIEW

The modification of ENR from NR was done by introducing oxygen atom to the unsaturated molecule of NR which is well known to react very readily with peracids[1]. The chemical reaction during epoxidation process will produce oxirane or epoxide compound that consists of three-membered ether (C-O-C) in a cyclic form (Figure 2.1).

Figure 2.1 The epoxidation of NR with peroxyacid

During the preparation of ENR, the epoxidation reactions are always accompanied with the further ring-opening reactions of epoxy groups[13]. Two major distinct ring opening products were obtained depending on the level of modification[4]. Majority of the epoxide groups at low level modification are isolated, hence the major products are trans-diol as proposed as Scheme 1 by I.R. Gelling (Figure 2.2). Dehydration of the tertiary alcohol also can occur.

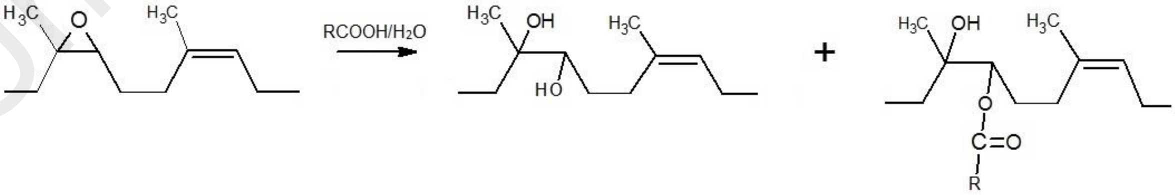


Figure 2.2 Secondary ring opening of epoxide groups (Scheme 1)

At high level modification, five-membered cyclic ether becomes the major product as illustrated in Figure 2.3 (Scheme 2).

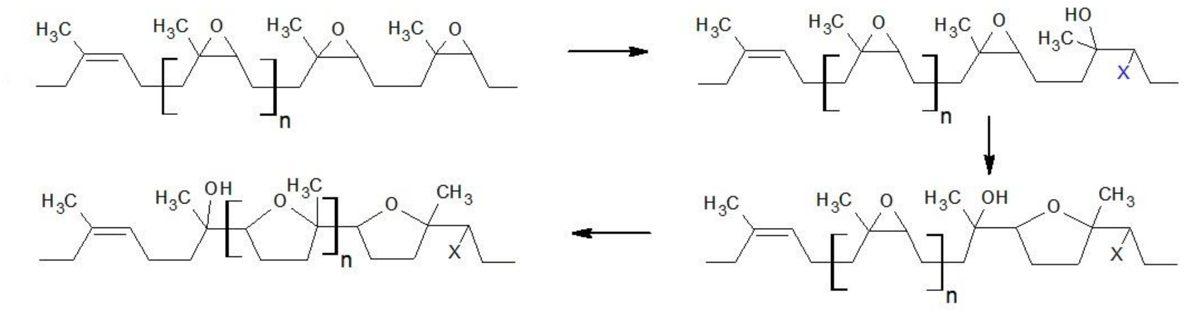


Figure 2.3 Ring opening of adjacent epoxide groups to yield five-membered cyclic ether (Scheme 2)

The mass-fraction of intermolecular ether increases as well which leads to the formation of gel (the insoluble part of rubber). Formation of ether crosslinks can occur in the acid catalysed ring opening of epoxides as proposed as Scheme 3[4] (Figure 2.4). The properties and applications of ENR will be affected by the presence of gel. High gel content in raw rubber will cause difficulty in processing especially in mixing or blending process[2].

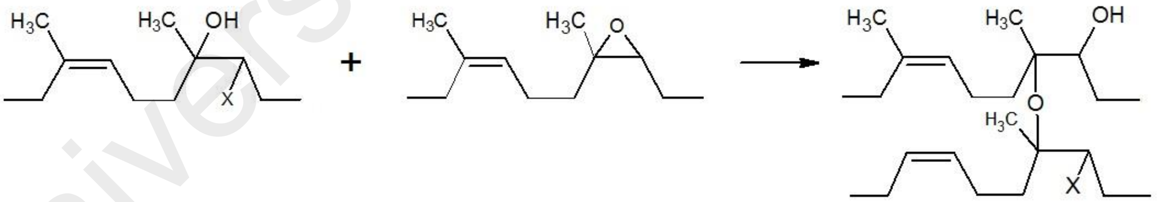


Figure 2.4 Crosslinking of ENR via ring-opened epoxide groups (Scheme 3)

A few grades of ENR are currently available depending on the extent of modification namely ENR 25 (25 mole % epoxide) and ENR 50 (50 mole % epoxide). There are various methods available for the quantification of epoxidation level namely elemental analysis (carbon, hydrogen and oxygen), infrared spectroscopy (IR), proton (^{1}H) and carbon (^{13}C) nuclear magnetic resonance spectroscopy (NMR) as well as chemical titrimetric technique.

For elemental analysis, the ENR sample must be dried under high vacuum at 333K to minimize the interferences from trace moisture and other volatile. The epoxy content was calculated from the %C analysis after making allowance for low levels of protein, as deduced from %N present[14].

For the measurement of epoxidation level using ^{1}H and ^{13}C NMR, deuterated solvent (e.g. deuterated chloroform) is used to dissolve the ENR prior to analysis. One-dimensional (1D) and two-dimensional (2D) experiments such as COSY, HETCOR, HMBC were also commonly perform to collect complex data and were Fourier-transformed in the absolute value mode. The epoxy group content of ENR was estimated from the intensity ratio of the signals at 2.7 ppm and 5.1 ppm as in the following equation;

$$X_{Epoxy} = \frac{I_{2.7}}{I_{2.7} + I_{5.1}} x\ 100$$

where I is the intensity of the signals and subscript numbers represent chemical shift (ppm)[15].

The determination of epoxidation level using FTIR for ENR rubber can be done directly by using attenuated total reflectance (ATR) technique. Alternatively, the rubber can be pyrolyzed and the pyrolyzate was transferred between a NaCl cell or KBr disc and subjected further to FTIR using absorbance mode[16]. In the case of ENR in latex form, it is coated onto a clean glass plate directly. The film was air dried, peeled carefully and scanned with FTIR[13]. The calculation of epoxidation level is deduced from Lambert-Beer Law as follows;

$$C_e = \frac{100k_1A_2}{A_1 + k_1A_2 + k_2A_3}$$

where;

$A_1 = A_{835}$

$A_2 = A_{870} – 0.14A_{835}$

$A_3 = A_{3460} – 0.019A_{1375}$

A_{835}, A_{870}, A_{1375} and A_{3460} are the absorbances corresponding to 835 cm^{-1}, 870 cm^{-1}, 1375 cm^{-1} and 3460 cm^{-1} respectively

The value of k_1 and k_2 were determined using NMR method

Chemical titrimetric technique for the determination of epoxidation level can be performed by a direct titration of epoxide ring with HBr in glacial acetic acid[14]. This technique has been shown to be essentially quantitative and exhibit few interferences for epoxidized polyisoprene at low modification level (<5 mol %). The HBr method is a rapid technique which is suitable for analysis of ENR in the region <15 mol % where the spectroscopic techniques such as NMR and FTIR are less accurate.

Two major distinct ring opening products were obtained depending on the level of modification. The various ring opening structures were widely investigated and characterized by a combination of Infrared (IR) and Nuclear Magnetic Resonance (NMR) spectroscopy[13,17,18].

Ionic liquids (ILs) are made up of cationic and anionic species. IL has high ionic character that enhances the reaction rates to a great extent in many reactions including microwave-assisted organic synthesis as well as polymerization reactions. The strength of the cation, the anion or combination of the cation and anion determined the acidity or basicity of ILs. The IL properties can be tailored by the combinations of these cations and anions. Anion is responsible for air and water stability properties and the cation responsible for melting temperature and organic solubilility. Common cations contain C1-C18 alkyl groups (e.g. ethyl, butyl and hexyl) derivatives of N-alkyl-N′-methylimidazolium and N-alkylpyridinium, pyrrolidinium, pyridazinium, pyrimidinium, pyrazinium, pyrazolium, triazolium, thiazolium and oxazolium. The examples of anions include carboxylates, fluorinated carboxylates, sulfonates, fluorinated sulfonates, imides, borates, phosphates, antimonates, halides, halometallates, etc.[19]. ILs are complex and versatile solvents capable to interact via hydrogen bonding, $\Pi - \Pi$, $n - \Pi$, dispersive, dipolar, electrostatic and hydrophobic interactions. These specific ILs may be utilized to dissolve a particular chemical or to extract a certain material from a solution[9].

Ionic liquids containing imidazolium cations such as 1-butyl-3-methylimidazolium chloride (BmimCl) and 1-ethyl-3-methylimidazolium acetate (EmimAc) have been widely used in dissolving biopolymers that are linked together by strong intermolecular hydrogen bonds such as cellulose, carbohydrates and chitosan[20,21,22,23,24,25].

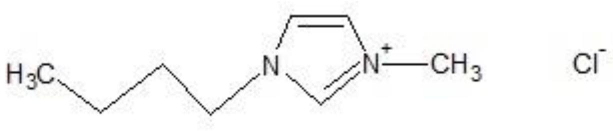


Figure 2.5 1-Butyl-3-methylimidazolium Chloride (BmimCl)

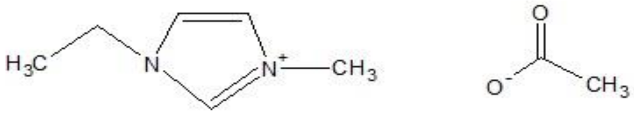


Figure 2.6 1-Ethyl-3-methylimidazolium Acetate (EmimAc)

The used of ILs in ENR application has revolved around polymer electrolyte system in enhancing ionic conductivity[10,11]. The study of variety of ionic liquids for the dissolution of cellulose is done to develop new processing technologies, cellulose functionalization methods and new cellulose materials (blends, composites, fibers and ion gels). However, there is not much investigation on the dissolution of the gel part of ENR using IL. Hence, the investigation on the suitable IL for dissolving the gel part of ENR was done by using similar approach used in dissolution of cellulose using IL.

Ionic liquids with halide anion (e.g. BmimCl) and other counter anions such as phosphate, formate and acetate have been studied quite extensively in the literature with the ability to efficiently dissolve cellulose[26]. In some of the studies, the solubility of cellulose in allyl-3-methylimidazolium chloride (AmimCl) at 80°C and 1-ethyl-3-methylimidazolium acetate (EmimAc) at 90°C were found to be 14.5 wt%[20] and 16 wt% (can be increased up to 25 wt% with microwave heatings)[26]. In 2002, Swatloski has screened 1-butyl-3-methylimidazolium cations ($Bmim^+$) with a range of anions such as Cl^-, PF_6, Br^-, SCN^- and BF_4^- in the dissolution of cellulose. It was observed that strong hydrogen bond acceptors anions (e.g. Cl^-) were the most effective solvents in dissolving cellulose, presumably solubilizing cellulose through hydrogen-bonding from hydroxyl functions to the anions of the solvent[22].

The possible dissolution mechanism of cellulose in IL[20] is shown in Figure 2.7. Anion and cation play important roles in the dissolution process. The cation and anion were separated at a certain temperature and able to form hydrogen bond with the cellulose. The hydrogen bond between cation/anion-cellulose was formed by destroying the intermolecular or intramolecular hydrogen bond within cellulose resulting in dispersion of cellulose molecules in IL. Organic solvent can be added as a co-solvent to improve the dissolution of cellulose in ionic liquid. The solvent power of the IL is enhanced by decreasing the duration for dissolution, even at low temperature [21].

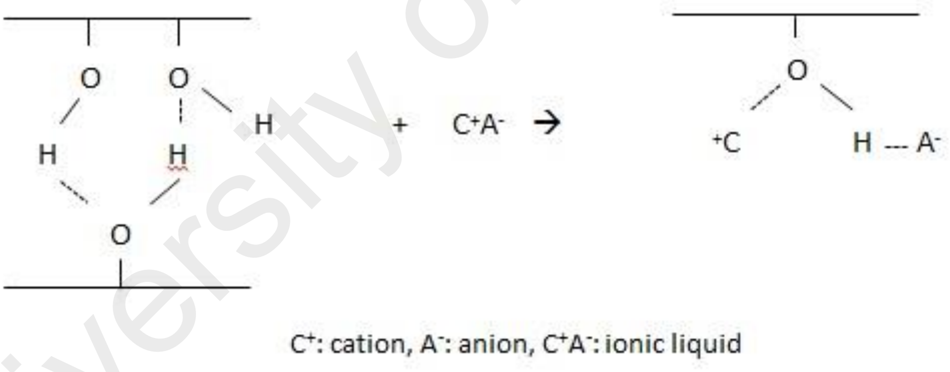


Figure 2.7 Possible dissolution mechanism of cellulose in IL

CHAPTER 3: METHODOLOGY

3.1 Preparation of ENR

Sample of ENR 25 and ENR 50 were supplied from Malaysian Rubber Board (MRB). They were prepared from LA-TZ latex concentrate by generating peroxy acid in situ technique from hydrogen peroxide and acid at the Rubber Research Institute of Malaysia (RRIM) pilot plant. The procedure and process parameters for the reaction are based on Gelling I.R. British Patent.

3.2 Determination of Gel Content

3.2.1 Determination of Gel Content using toluene, tetrahydrofuran (THF), chloroform and ethanol

About 0.2 g of finely cut rubber is weighed and placed in a stoppered bottle. 100 ml of Toluene (AR grade) was pipetted into the bottle and was kept for 48 hours with occasional shaking. The soluble part was filtered through 100 mesh steel gauze sieve, leaving the swollen rubber. The excess solvent was removed by touching the bottom of the filter with tissue paper and the weighing of wet gel was done immediately. The sample was dried in an air-circulating oven at 60°C for 16 - 24 hours. The sample was then placed in a desiccator for cooling before the dry weight was recorded. Gel content was calculated as percentage of the dried content to the weight of sample. The same procedure was applied using other solvents (THF, Chloroform and Ethanol).

3.2.2 Determination of Gel Content using (Toluene+BmimCl), (THF+ BmimCl) and (THF+EmimAc)

The ratio of IL to ENR used in this experiment was 1:0.5 (w/w). About 0.2 g of finely cut rubber is weighed and placed in a stoppered bottle. 100 ml of Toluene (AR grade) was pipetted into the bottle. 0.1 g of BmimCl was carefully weighed, transferred into the bottle and stirred. It was kept for 48 hours with occasional shaking. The soluble part was filtered through 100 mesh steel gauze sieve, leaving the swollen rubber. The excess solvent was removed by touching the bottom of the filter with tissue paper and the weighing of wet gel was done immediately. The sample was dried in an air-circulating oven at 60°C for 16 - 24 hours. The sample was then placed in a desiccator for cooling before the dry weight was recorded.

Leaching process was done by immersing the sieve containing dried gel in distilled water for 30 minutes at room temperature. The sample was dried in an air-circulating oven at 60°C for 2 hours. The leaching and drying steps were repeated 3 times until constant weight is achieved. Gel content was calculated as percentage of the dried content to the weight of sample. The same procedure was applied to other solvents (THF+BmimCl and THF+EmimAc).

3.3 Nuclear Magnetic Resonance (NMR) of proton (^{1}H) and carbon (^{13}C) of ENR (raw) and Dried gel of ENR

20-30 mg of sample was weighed and placed into the specimen vial. A pasteur pipette was used to transfer approximately 2 ml of deuterated chloroform solvent ($CDCl_3$) into the specimen vial. The specimen vial was left in the ultrasonic bath for approximately 5 minutes. The sample was kept in the specimen vial for 16-24 hours in a dark. Approximately 1 ml of the solution was transferred into the 5 mm NMR tube. The NMR tube was sealed with the tube stopper and the epoxidation and ring opening level were determined using Bruker AMX 400 Wide Bore NMR Spectrometer (400 MHz) using Tetramethylsilane (TMS, $\delta = 0.0$ ppm) as the internal standard. The percentage of epoxidation and ring opening were calculated from the integration of the areas under those peaks.

3.4 Fourier Transform Infrared (FTIR) - Attenuated Total Reflectance (ATR) of ENR (raw) and Dried Gel of ENR

The sample was directly placed on the top plate mounted in the sample beam of the spectrometer. The spectrum was then recorded over the nominal range 4000 - 400 cm^{-1}. The measurements were completed within 30 seconds and ATR spectrum was obtained.

3.5 Differential Scanning Calorimetric of ENR (raw) and Dried gel of ENR

About 1 – 10 mg of rubber was weighed placed in a crucible. The sample must has maximum contact with the bottom of the crucible by pressing down the sample using the tool available, or making the bottom surface as flat as possible. The crucible was sealed to prevent spilling of sample on the sensor and also to facilitate the robot operation. The rubbers were analyzed using DSC from -80°C to 20°C at a rate of 10 °C/min under nitrogen atmosphere to estimate the glass transition temperature (T_g).

CHAPTER 4: RESULTS AND DISCUSSION

4.1 Preliminary Study

The analysis was initiated by characterizing SMR CV and two grades of widely used ENR in the market namely ENR 50 and ENR 25 via FTIR, NMR and DSC. A rubber which exhibit low gel content and constant viscosity is required to be treated as a control sample. There is an established correlation between secondary ring openings for each grade of ENR where the increase in percentage of acid brought about an increase in the Mooney viscosity (V_R) and gel content values[6]. Hence, natural rubber with constant viscosity (SMR CV) was chosen as a control sample in this experiment.

4.1.1 FTIR analysis

For SMR CV, the peaks at 3000 – 2800 cm^{-1} indicate the presence of methyl and methylene groups from the molecular backbone of NR (Figure 2.1). The peaks at 1662 cm^{-1} and 838 cm^{-1} are assigned to the C=C bonds and =CH of NR respectively (Figure 4.1).

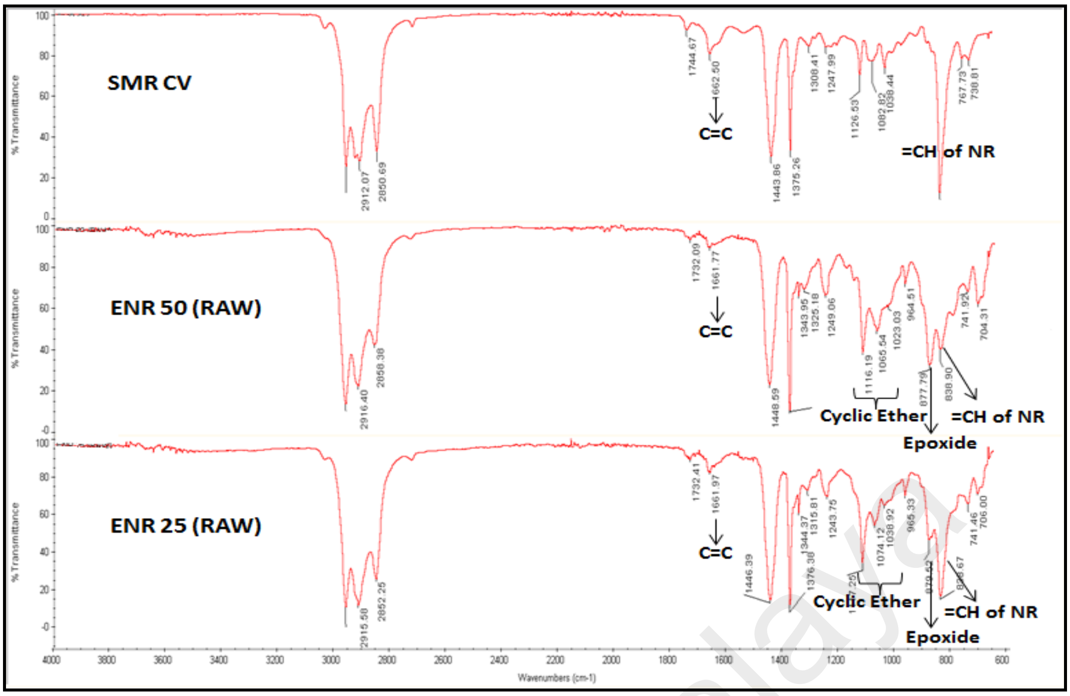


Figure 4.1 FTIR Spectrum of SMR CV, ENR 50 (Raw) and ENR 25 (Raw)

The modification process of ENR from NR was done by introducing oxygen atom to the unsaturated molecule of NR which is well known to react very readily with peracids. The chemical reaction during epoxidation process will produce oxirane or epoxide compound that consists of three-membered ether in a cyclic form (Figure 2.1). Therefore, the emergence of absorption signal at 877 cm^{-1} which is related to epoxide of ENR is observed in the FTIR spectrum. ENR 50 exhibits a very intense signal at 877 cm^{-1} due to higher epoxidation level as compared to ENR 25. Additional absorption signals at approximately 1116 – 1075 cm^{-1} indicate the presence of cyclic ether. The observed characteristic absorption signals were consistent with those reported in previous works[4,27]. The characteristic absorption signals of ENR are listed in Table 4.1.

Table 4.1 Functional Group from ENR spectrum

Functional group	Peak Max (cm^{-1})
Epoxide of ENR	877
=CH of NR	837
Cyclic ether	1116 – 1075
C=C of NR	1662
CH_2, CH_3	3000 - 2800

4.1.2 NMR analysis

SMR CV and both grades of ENR were characterized by ^{1}H NMR and ^{13}C NMR. The results are represented in Figure 4.2. For SMR CV, three signals characteristics of methyl, methylene and unsaturated methine proton of cis-1,4-isoprene appeared at 1.67, 2.04 and 5.13 ppm respectively. Epoxidation leads to a very significant shift of the methyl protons, the disappearance of methylene proton of isoprene and the appearance of a methine resonance due to the epoxy ring[6]. Two signals characteristic of epoxy group appeared at 1.31 and 2.72 ppm which were assigned to methyl and methine proton of epoxy group. The observed NMR spectrum match those from the literatures[4,17,27,28]. For the determination of epoxidation level, the integrations were done for the methylene proton of isoprene (δ = 5.3 - 5.0 ppm) and epoxy methine protons (δ = 2.9 - 2.6 ppm). The determination of ring opening were done by taking into account the integrated peak at δ = 3.5 - 3.2 ppm and δ = 4.0 - 3.7 ppm. The epoxidation level (E%) and ring opening values (RO%) for ENR 25 and ENR 50 are E_{25} = 26.6%; RO_{25} = 0.39% and E_{50} = 50.5%; RO_{50} = 1.1% respectively.

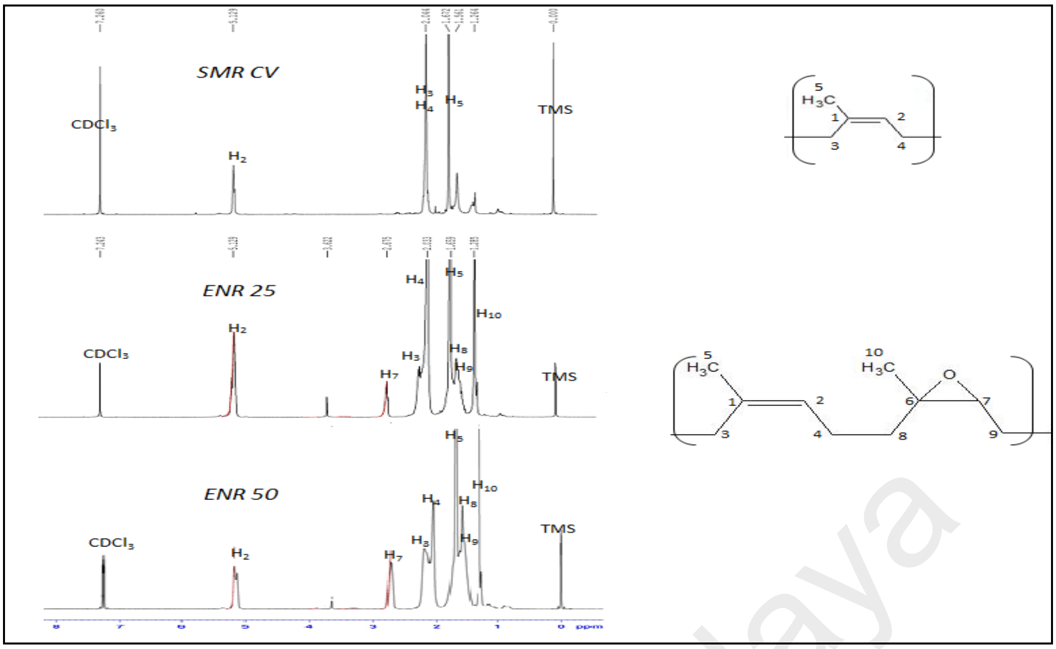


Figure 4.2 ^{1}H NMR spectrum of SMR CV, ENR 25 and ENR 50 (raw rubber)

To confirm the assignment, ^{13}C NMR measurement was done for both ENR 25 and ENR 50. Upon epoxidation process, many signals appeared in the aliphatic region and two signals appeared at 60 ppm and 64 ppm which are attributed to carbon A and carbon B from the epoxy ring (Figure 4.3). The signals at 125 ppm and 64 ppm are assigned to methine carbon of isoprene unit and the epoxidized isoprene unit[15].

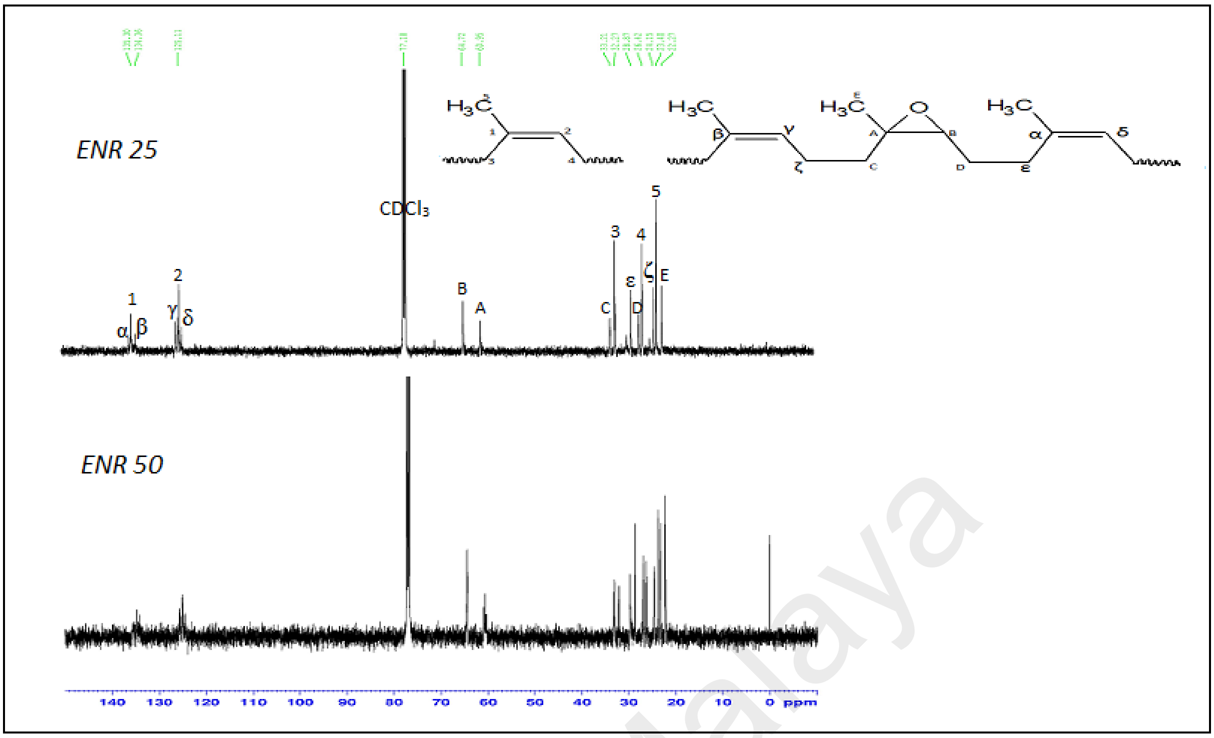


Figure 4.3 ^{13}C NMR spectra of SMR CV, ENR 25 and ENR 50 (raw rubber)

4.1.3 DSC analysis

Glass Transition Temperature (T_g) is the temperature at which it changes from a glass to the rubbery form. At low temperature the amorphous regions of a polymer are in the glassy state. If the polymer is heated it eventually will reach its T_g. At this temperature the polymer is in its rubbery state where the rubber is soft and flexible. Determination of T_g by DSC is commonly practiced in the investigation of phase behaviour of the polymer. The rubbers were exposed to specific thermal procedure as described in 3.5 for T_g estimation. The T_gs of the rubbers are summarized in Table 4.2.

Table 4.2 Glass Transition Temperatures (T_g) of SMR CV, ENR 25 and ENR 50

Rubber	Onset Temperature (°C)
SMR CV	-65.5
ENR 25	-45.3
ENR 50	-25.1

SMR CV exhibit T_g at a low temperature range (-65.5°C). Epoxidation results in a systematic increase in the polarity and T_g. Epoxidation process will produce oxirane or epoxide compound that consists of three-membered ether in a cyclic form. The epoxide rings in the polymer chain reduces the flexibility of the chain and raise the value of T_g (Figure 4.4). Hence, the increase in T_g value of ENR 25 as compared to SMR CV can be explained on the basis of this process. ENR 50 exhibit higher T_g than ENR 25 due to presence of more epoxide ring in the polymer chain.

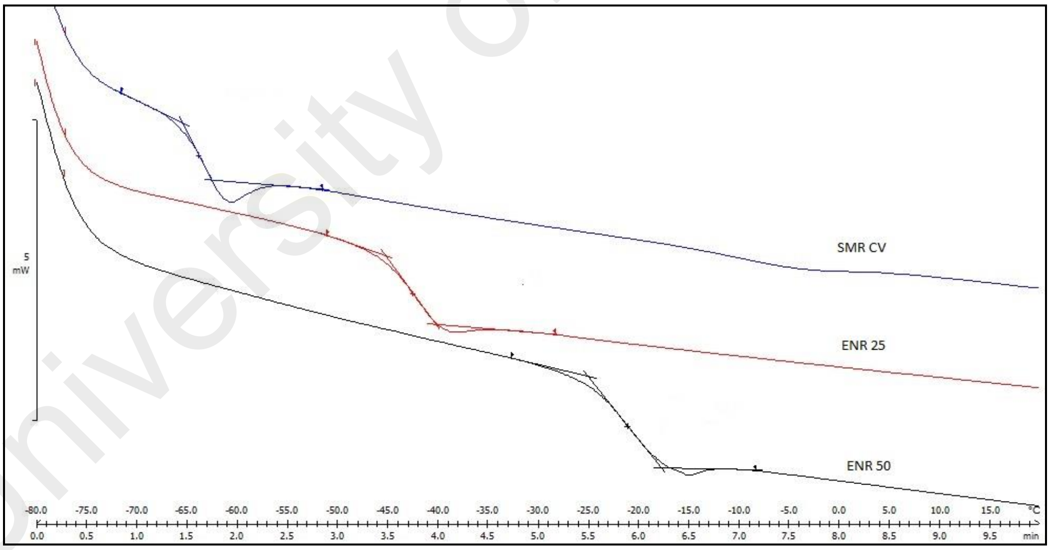


Figure 4.4 DSC thermogram of SMR CV, ENR 25 and ENR 50 (raw rubber)

4.2 Gel Content Analysis

4.2.1 Gel Content of SMR CV, ENR 25 and ENR 50

Four types of solvents namely toluene, tetrahydrofuran (THF), ethanol and chloroform ($CHCl_3$) were used in the gel content analysis of SMR CV, ENR 25 and ENR 50. Currently, there is no standard test method for the determination of gel content specifically for ENR. In a previous study, ISO test method entitled ISO 17278:2013 Rubber, Raw Natural – Determination of the Gel Content of Technically Specified Rubber (TSR) is used to determine gel content of ENR; however, the repeatability is not satisfactory and produces inconsistent gel content values. Hence, in-house test method developed by Malaysian Rubber Board (MRB) is used in this experiment. Gel content was calculated as percentage of the dried content to the weight of sample as follows;

$$\%\ of\ Macro\ gel\ Content = \frac{Weight\ of\ dry\ rubber}{Weight\ of\ Sample} X\ 100$$

The analysis is initiated by soaking SMR CV in two different solvents (toluene and THF) and left for 48 hours. The sample is then filtered and dried in an oven before the final weight is recorded. Almost complete dissolution of SMR CV in both solvents is observed. The mean percentages of macro gel for SMR CV soaked in toluene and THF are 1.19% and 1.53% respectively with a very small differences recorded between two readings.

ENR 25 and ENR 50 which were soaked in toluene, THF and chloroform demonstrated quite similar mean percentage of macro gel which is ranging from 42.07%

to 45.19%. This indicates that the used of different solvents did not give any effect on the gel content values. Both ENR 25 and ENR 50 exhibit high gel content regardless of types of solvent used. This will lead to the assumption that species other than epoxide is present. Chemical crosslinking may occur due to an epoxy ring-opening reaction, which leads to a secondary reaction and forming gel[22]. Complete dissolution process can happen when the solute-solvent forces of attraction are great enough to overcome the solute-solute and solvent-solvent forces of attraction. In this process, soluble parts of ENR were solvated by molecules of solvents and thus able to be diffused out of the gel network. In the case of ethanol, both ENR 25 and ENR 50 cannot be dissolved where the rubbers were still intact even after being soaked for 48 hours. The percentages of macro gel for SMR CV, ENR 25 and ENR 50 in various solvents are tabulated in Table 4.3.

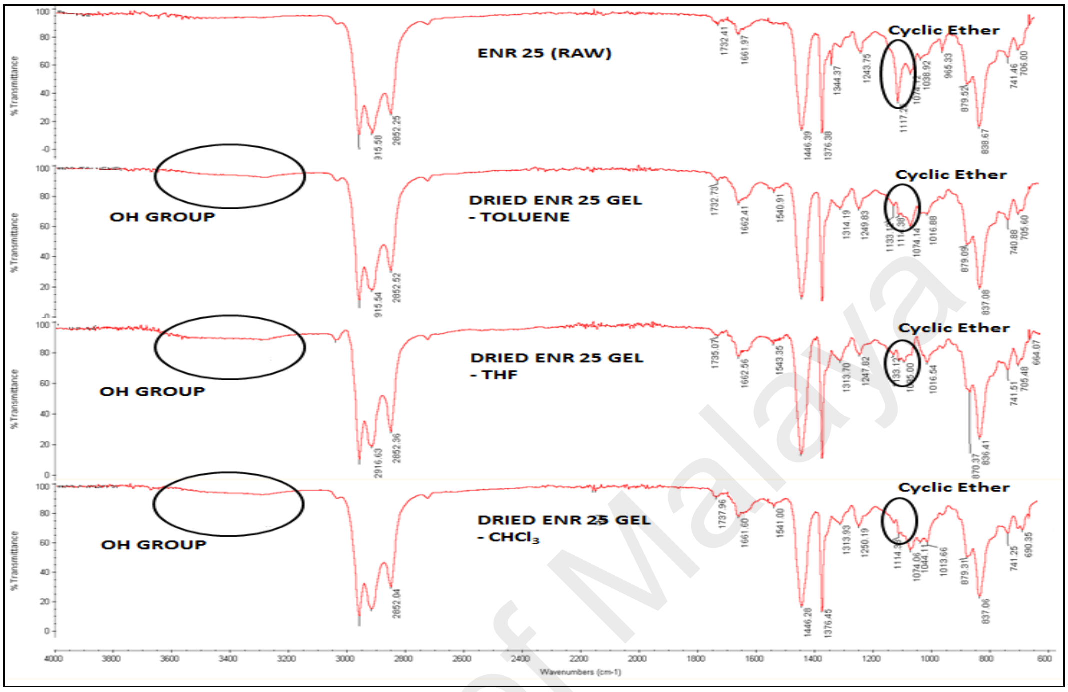
Table 4.3 Percentage of Macro Gel of SMR CV, ENR 25 and ENR 50 in Various Solvents

Rubber	Solvent	Macro gel, %	Macro gel, % (Average)
SMR CVa SMR CVb	THF	1.53 1.53	1.53
SMR CVa SMR CVb	Toluene	1.19 1.19	1.19
ENR 25a ENR 25b	Toluene	43.13 43.32	43.22
ENR 50a ENR 50b		42.52 43.78	43.15
ENR 25a ENR 25b	THF	44.58 43.84	44.21
ENR 50a ENR 50b		44.15 43.02	43.58
ENR 25a ENR 25b	Ethanol	Not dissolved in Ethanol	
ENR 50a ENR 50b			
ENR 25a ENR 25b	CHCl3	44.17 44.56	44.36
ENR 50a ENR 50b		43.75 43.31	43.53

4.2.2 Characterization of Dried Gel of ENR 25 and ENR 50

The dried gel of ENR was analysed using FTIR to identify the occurrence of any additional absorption signal that might attributed to ring opening or crosslinking of the structure by comparing with the spectrum of raw ENR. It was observed that the dried ENR gel which was dissolved in the three solvents show decreasing in the intensity of absorption signal at 1116 - 1074 cm^{-1} which is attributed to cyclic ether as illustrated in Figure 4.5. The decreasing trend is might be due to the opening up of the epoxy group of rubber and lead to the formation of ring opening product such as hydroxyl group.

This is supported by the occurrence of broad weak intensity absorption signal which is associated to OH stretching at 3400 cm^{-1} for both ENR 25 and ENR 50.



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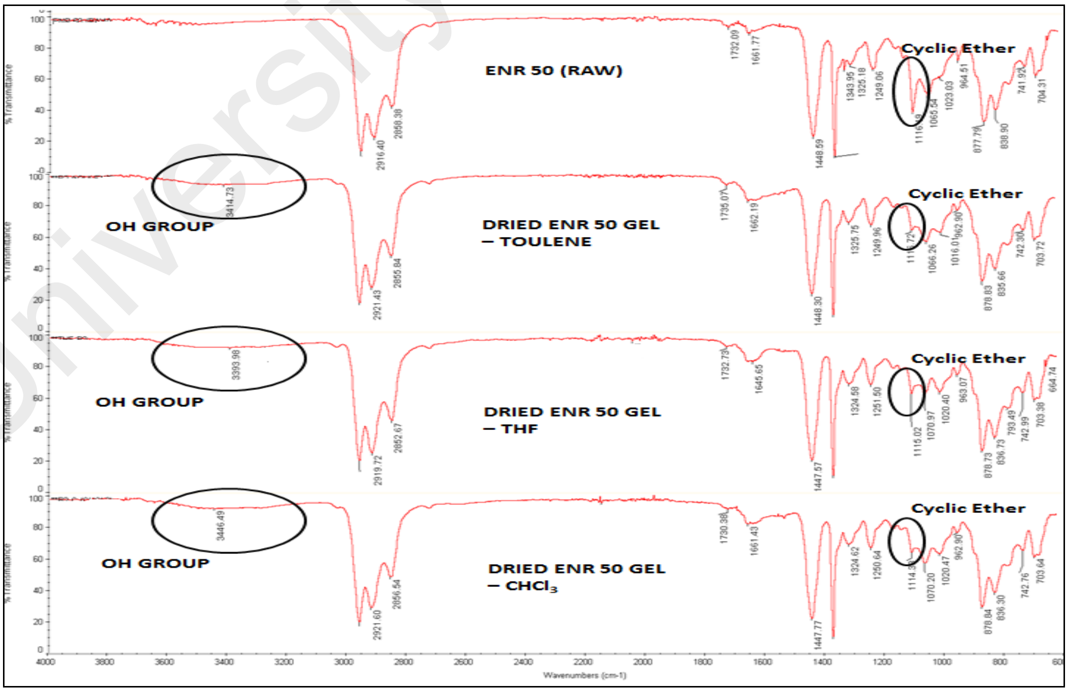


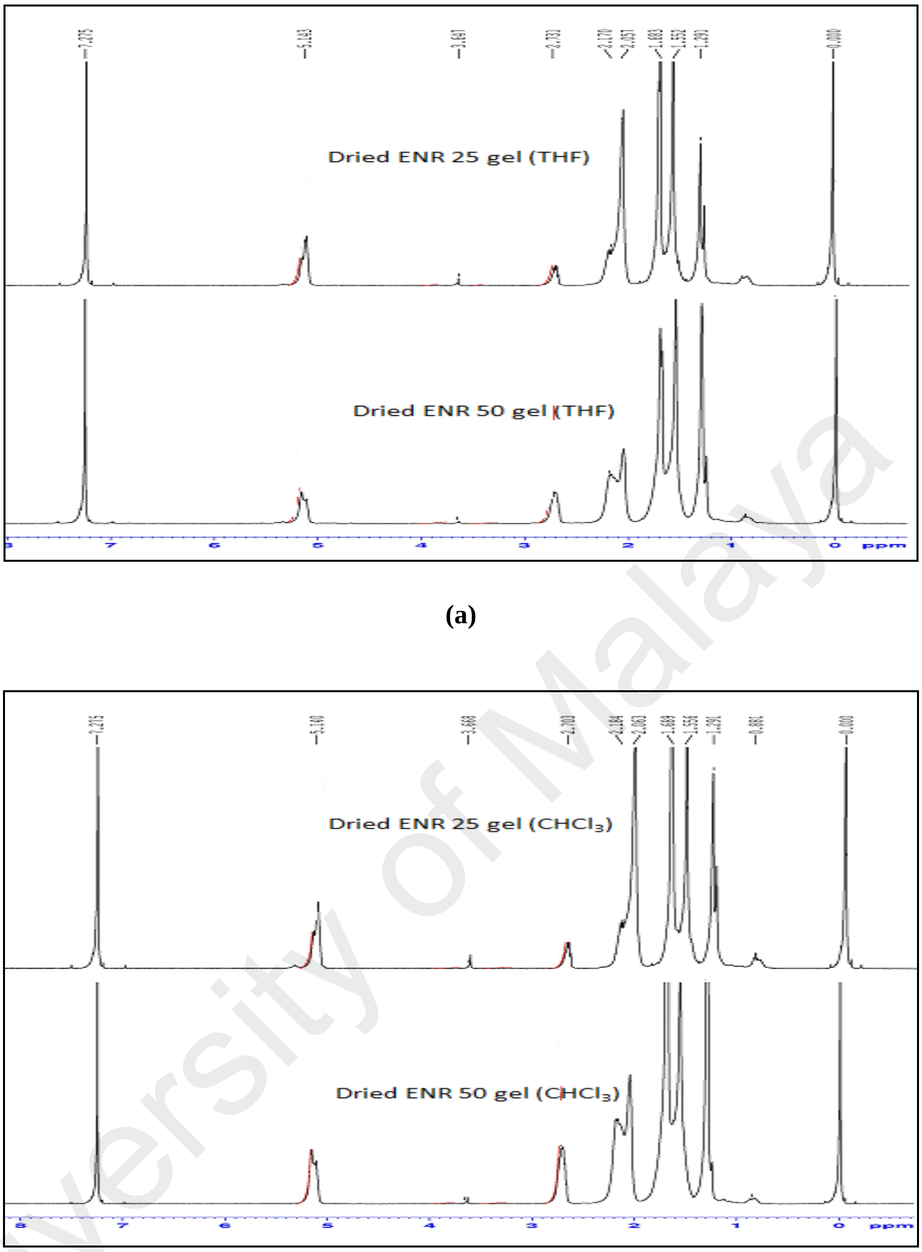
(b)

Figure 4.5 Reduction of intensity of cyclic ether peak and occurrence of OH group in dried ENR gel (toluene, thf and chloroform) for (a) ENR 25 and (b) ENR 50

The dried ENR 25 and ENR 50 were analyzed using ^{1}H NMR to identify the presence of peak which can be correlated to ring opening in the structure which related to gel formation. The gel from toluene analysis yield a very small amount of dried gel and it was quite difficult to collect the sample for further analysis. Therefore, the dried gel obtained from THF and chloroform was further subjected to ^{1}H NMR analysis. The dried ENR gel is dissolved in deuterated chloroform (*d*-chloroform) prior to ^{1}H NMR analysis. There is no significant difference in the epoxidation level and ring opening values of the dried ENR gel from the raw ENR as tabulated in Table 4.4 and illustrated in Figure 4.6.

Table 4.4 Epoxidation and Ring Opening Level of ENR (raw) and Dried ENR Gel

Solvent used for gel content determination	ENR	Epoxidation level (%)	Ring Opening (%)
Nil	ENR 25 (Raw)	26.6	0.4
	ENR 50 (Raw)	50.5	1.1
THF	Dried ENR 25 gel	27.4	1.6
	Dried ENR 50 gel	50.0	0.4
$CHCl_3$	Dried ENR 25 gel	26.9	1.0
	Dried ENR 50 gel	51.3	0.8



(a)

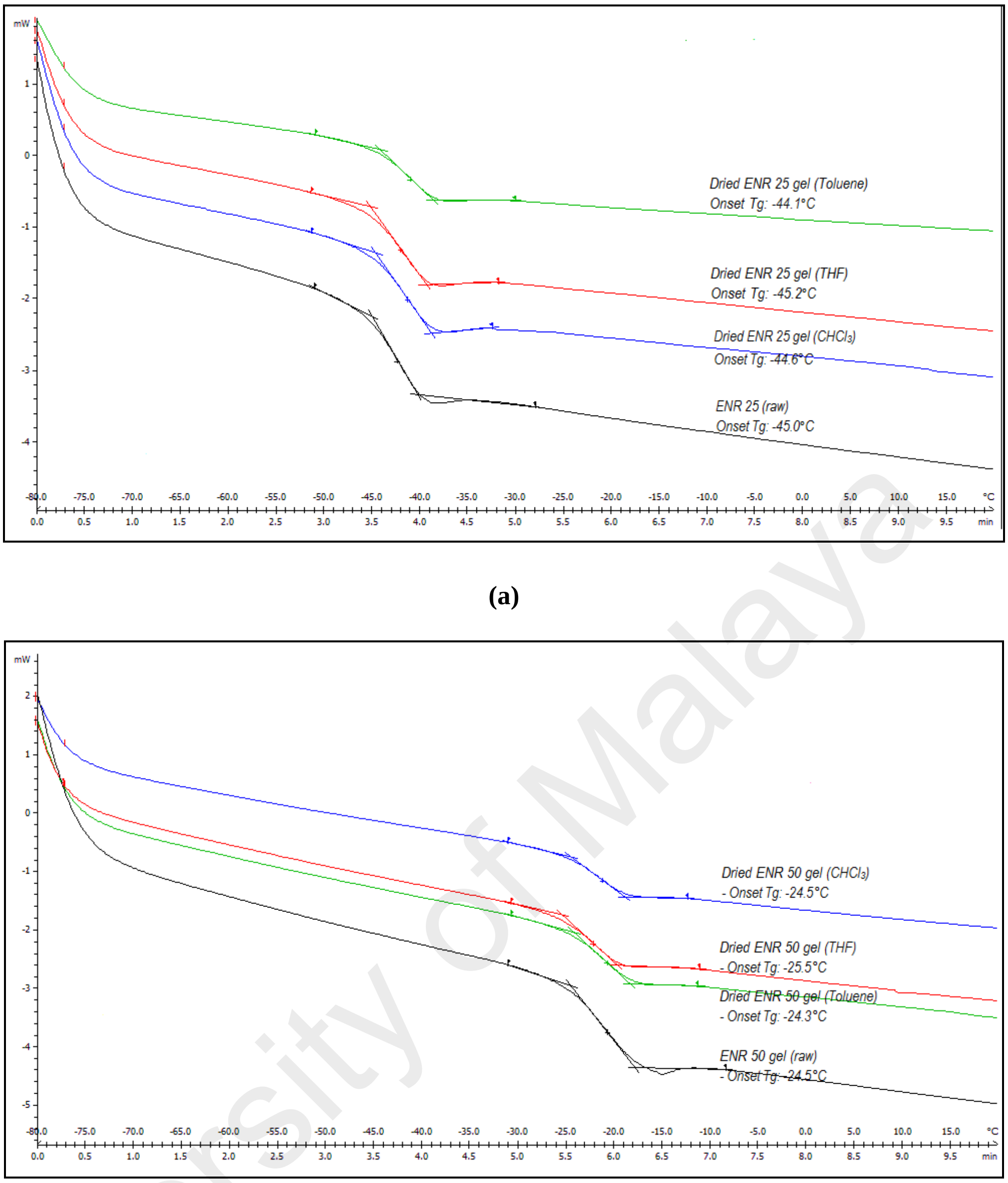
(b)

Figure 4.6 ^{1}H NMR Spectrum of Dried ENR 25 Gel and Dried ENR 50 Gel (a) THF and (b) chloroform

Since there is a decrease in the intensity of cyclic ether peak which is due to the ring opening of the epoxy group, the DSC analysis was carried to investigate any changes on the T_g values. Epoxide ring opening reactions via ether crosslinks resulted the increase in T_g and crosslink density as reported by Gabriel O. Shonaike and George P. Simon[29]. In this study, we found a slight shift of T_g to higher temperature for the dried ENR 25 and ENR 50 gel as compared to the respective raw ENRs as tabulated and illustrated in Table 4.5 and Figure 4.7. Another possibility is due to the ratio of ether crosslink present in the ENR is too little, therefore the restriction in the molecular motion is undetectable by DSC.

Table 4.5 Glass Transition Temperatures (T_g) of Dried ENR 25 gel and Dried ENR 50 gel

Rubber	Solvent	Onset T_g (°C)
ENR 25	ENR 25 (raw)	-45.0
	Toluene	-44.1
	THF	-45.2
	Chloroform	-44.6
ENR 50	ENR 50 (raw)	-24.5
	Toluene	-24.3
	THF	-25.5
	Chloroform	-24.5



(a)

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Figure 4.7 DSC thermogram of (a) Dried ENR 25 gel and (b) Dried ENR 50 gel

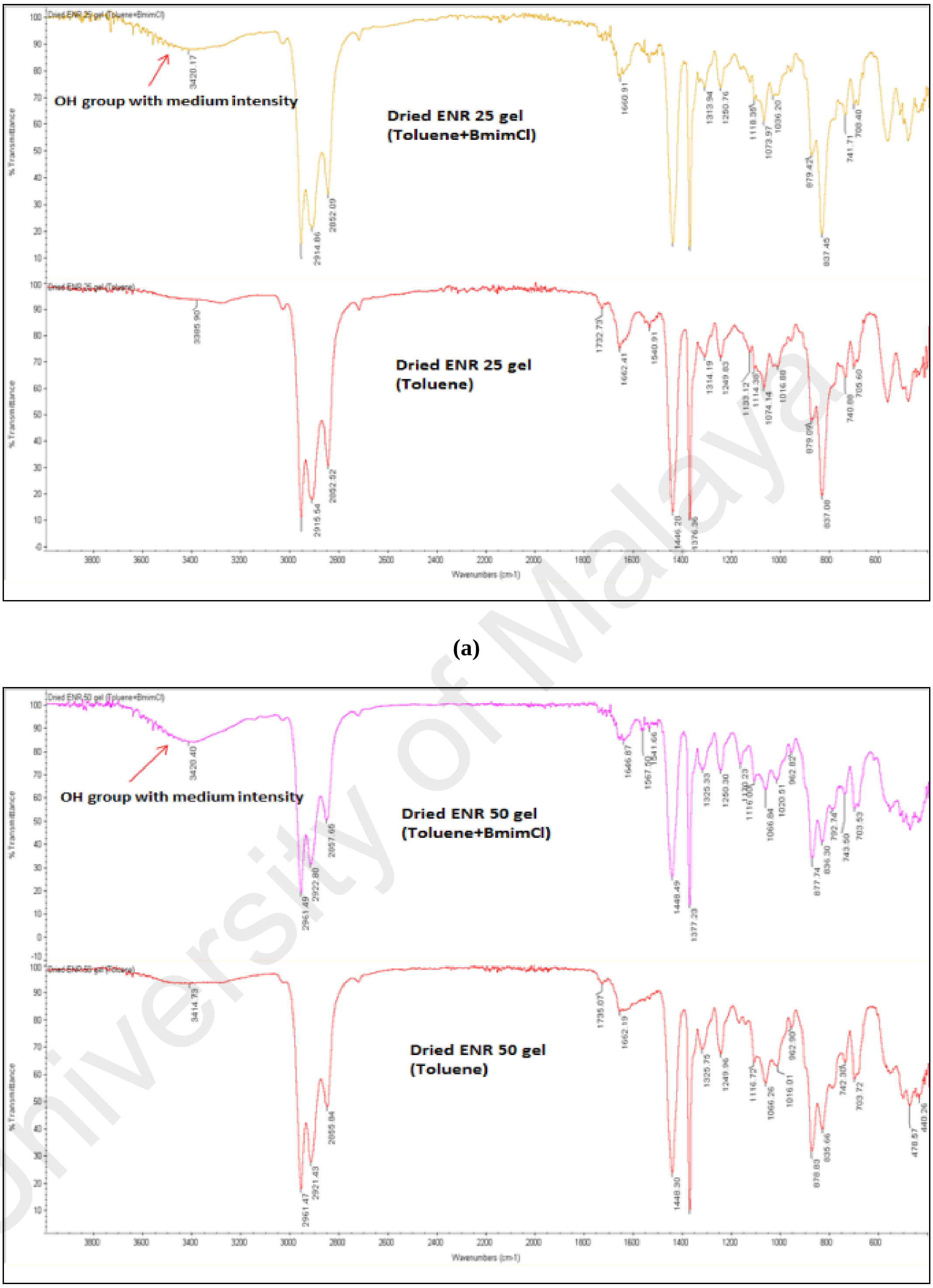
4.2.3 Gel Content Analysis - (Toluene+BmimCl)

To study the solubility of ENR in solvent, 1-butyl-3-methylimidazolium chloride (BmimCl) was added during gel content analysis in order to see the potential of ionic liquid in assisting the dissolution process of rubber**.** The incorporation of BmimCl during soaking of rubber with toluene has resulted in slightly higher mean swelling ratio and gel content values for SMR CV. There is no significant weight reduction between the weight after filtration (weight of wet rubber) and the final weight (weight after dried in an oven). This might be due to the incomplete drying of the gel before the final weighing which resulted in inconsistency in the gel measurement. Hence, increasing trends were observed for the mean percentage of macro gel for both ENR 50 and ENR 25 with a large standard deviation recorded between replication as listed in Table 4.6.

Table 4.6 Percentage of Macro Gel of SMR CV, ENR 50 and ENR 25 in Toluene+BmimCl

Rubber	Solvent	Macro gel, % (Average)	Macro gel, % (SD)
SMR CV	BmimCl +Toluene	15.81	8.52
ENR 25		62.38	1.44
ENR 50		65.24	14.10

The dried ENR 50 and ENR 25 gel were further analysed using FTIR. A broad medium intensity of absorption signal at 3400 cm^{-1} is observed due to the quarternary amine salt formation with the chlorine from the BmimCl[30]. There is a possibility of overlapping of quarternary amine and OH group in this region (Figure 4.8).



(a)

(b)

Figure 4.8 OH Group with Broad Medium Intensity Peak for (a) Dried ENR 25 Gel and (b) Dried ENR 50 Gel

C-N stretching vibration at approximately 840 cm^{-1} was unable to be detected due to the possible overlapping with =CH of NR absorption signal. Appearance of absorption signal at 1175 cm^{-1} is suspected to be due to the C-N group of the BmimCl. A small absorption signal is observed, but it is sufficient to indicate a new signal is present for ENR 25 while more intense signal is observed for ENR 50 (Figure 4.9).

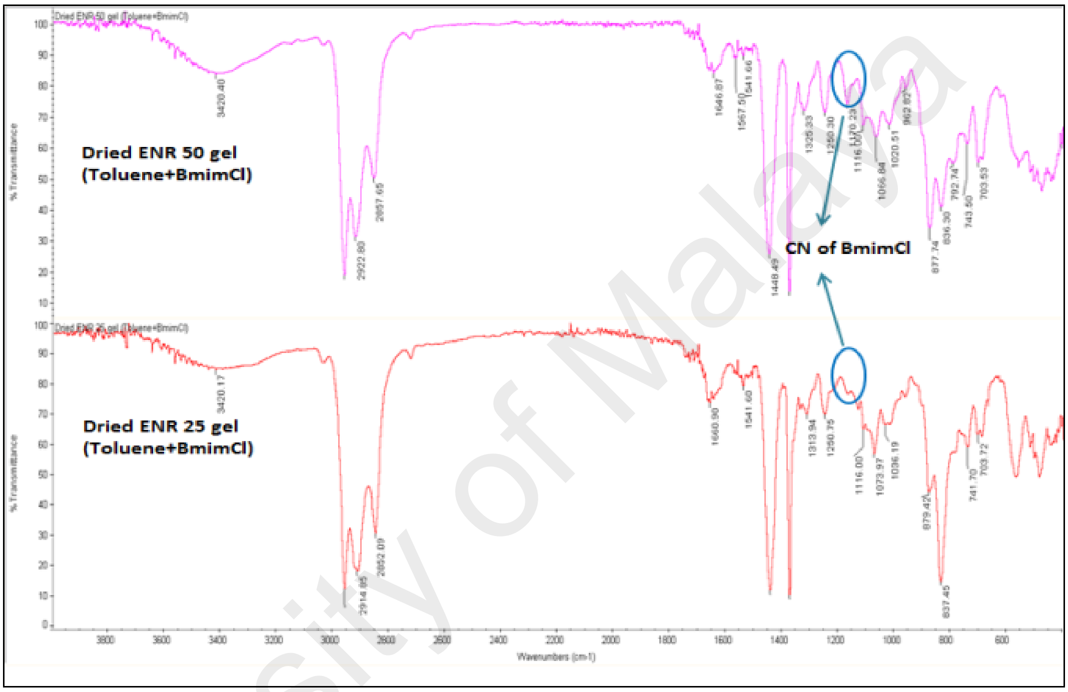


Figure 4.9 CN Group of the BmimCl for Dried ENR 50 & 25 Gel

4.2.4 Gel Content Analysis - (THF+BmimCl) and (THF+EmimAc)

The gel content analysis was carried out using THF with the incorporation of BmimCl and EmimAc. Since there is no significant weight reduction between the weight after filtration (weight of wet rubber) and the final weight (weight after dried in an oven) due to incomplete drying of the gel as observed in toluene, a leaching step was added into the process to leach out the excess IL. Distilled water is used during the leaching process due to the hygroscopic nature of IL. A series of leaching and drying steps were carried out and final weighing was recorded for every subsequent step. No heat is involved in the leaching process to minimize any interference during gel content determination.

The incorporation of BmimCl and EmimAc during soaking of SMR CV with THF has resulted slightly lower gel content values after the completion of third leaching cycle with a small deviation recorded between replication. This is a good indicator that both ILs have potential in assisting the dissolution process where soluble parts of NR were solvated by molecules of solvents and thus able to be diffused out of the gel network. This might be due to the very low gel content exhibit by the SMR CV. This has been discussed in Page 20 where almost complete dissolution of SMR CV in THF is observed. The mean percentages of macro gel for SMR CV soaked in THF is 1.53% with a very small differences recorded between two readings.

Increasing trend of macro gel value of ENR 25 (THF+BmimCl) as compared to ENR 25 (THF) was observed. On the other hand, the macro gel value of ENR 50 (THF+BmimCl) is comparable with ENR 50 (THF). Both ENR 25 and ENR 50 dissolved in THF+EmimAc showed lower macro gel values after third leaching cycle with a large standard deviation recorded between replication for ENR 50 as listed in Table 4.7 and Table 4.8. Even though there is significant weights reduction between the weight after filtration (weight of wet rubber) and the final weight (weight after dried in an oven), the inconsistency in the gel content values were found that may cause by the inefficient leaching process. This limitation can be overcome by improving the leaching technique.

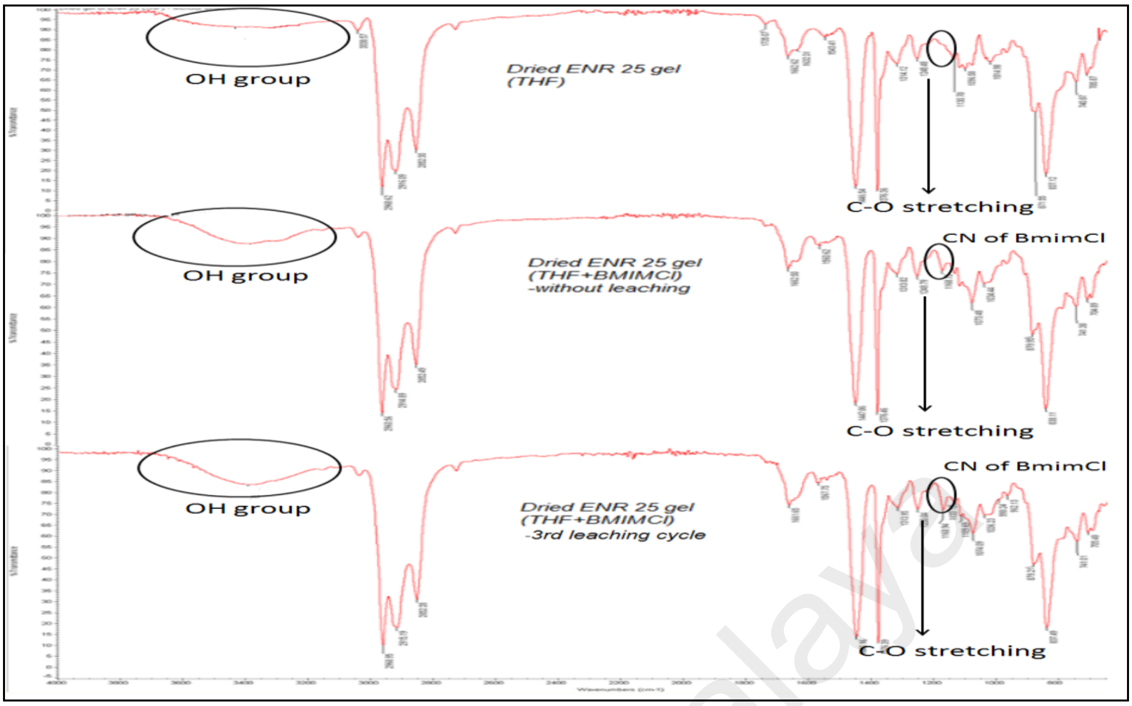
Table 4.7 % Macro gel of ENR dissolved in THF+ BmimCl

RUBBER	***% of Macro gel***					
	THF	***THF+BmimCl***				
		Without Leaching	1st leaching cycle	2nd leaching cycle	3rd leaching cycle	
SMR CV	1.53	22.28 8.02	1.13 0.33	0.93 0.45	1.02 0.30	*Mean* *SD*
ENR 25	44.21	78.34	48.35	47.55	47.50	
ENR 50	43.58	68.55	43.55	42.96	43.15	

Table 4.8 % Macro gel of ENR dissolved in THF+EmimAc

RUBBER	***% of Macro gel***					
	THF	***THF+EmimAc***				
		Without Leaching	1st leaching cycle	2nd leaching cycle	3rd leaching cycle	
SMR CV	1.53	9.81 1.76	0.81 0.35	0.60 0.23	0.55 0.28	*Mean* *SD*
ENR 25	43.84	55.12 4.55	42.82 2.88	43.16 0.12	42.89 0.16	*Mean* *SD*
ENR 50	44.15	52.32 19.63	35.94 17.22	37.50 24.11	37.26 23.97	*Mean* *SD*

FTIR and NMR analysis were carried out to confirm the effectiveness of leaching process to remove the excess BmimCl and EmimAc. Appearance of absorption at 1175 cm^{-1} which is corresponded to the C-N group of the BmimCl and EmimAc is still present even after the third leaching cycle (Figure 4.10 and Figure 4.11).



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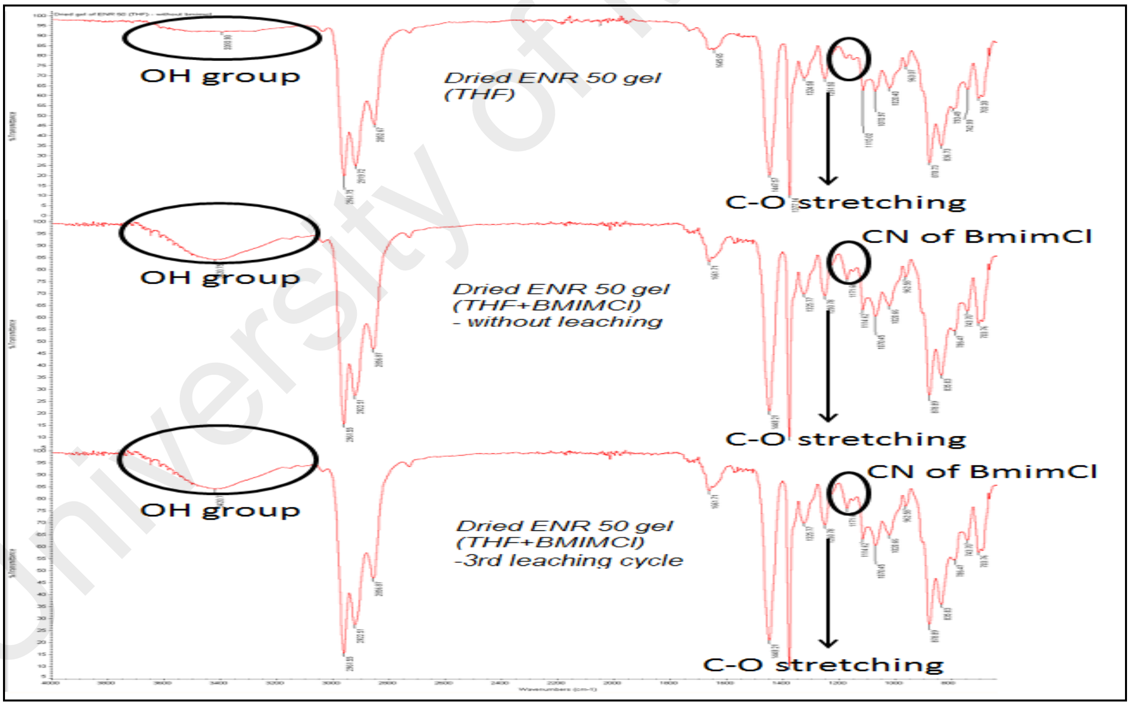
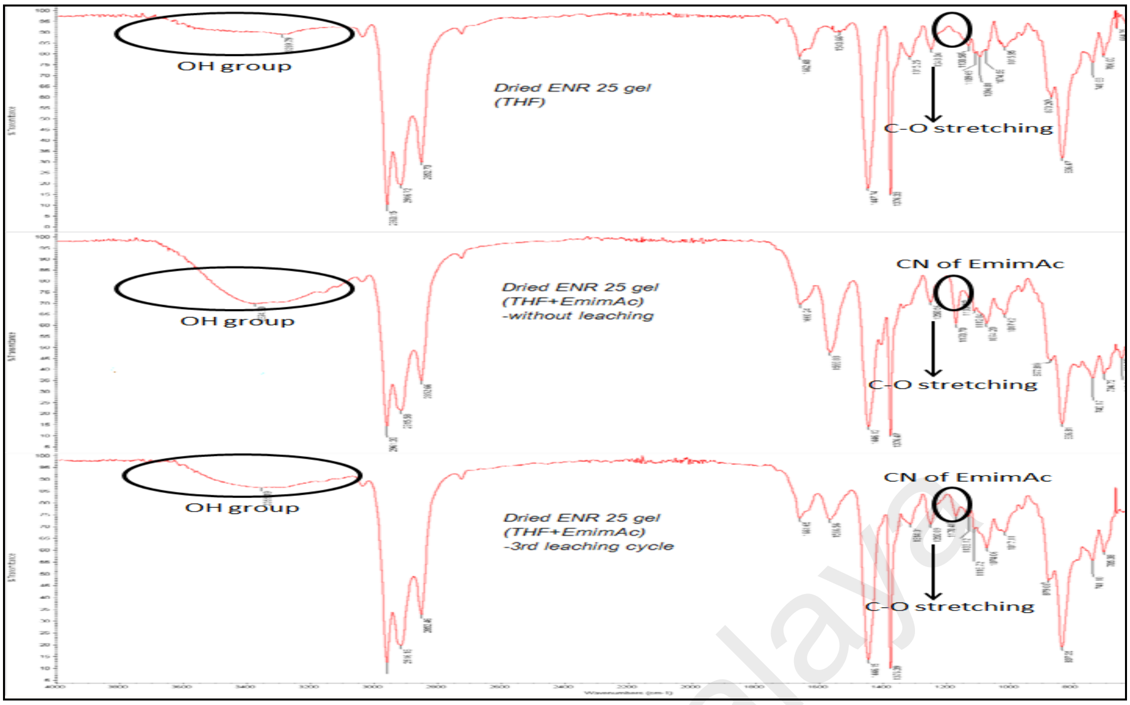


(b)

Figure 4.10 Increased peak intensity of OH and CN group for (a) Dried ENR 25 Gel (THF+BmimCl) and (b) Dried ENR 50 Gel (THF+BmimCl)



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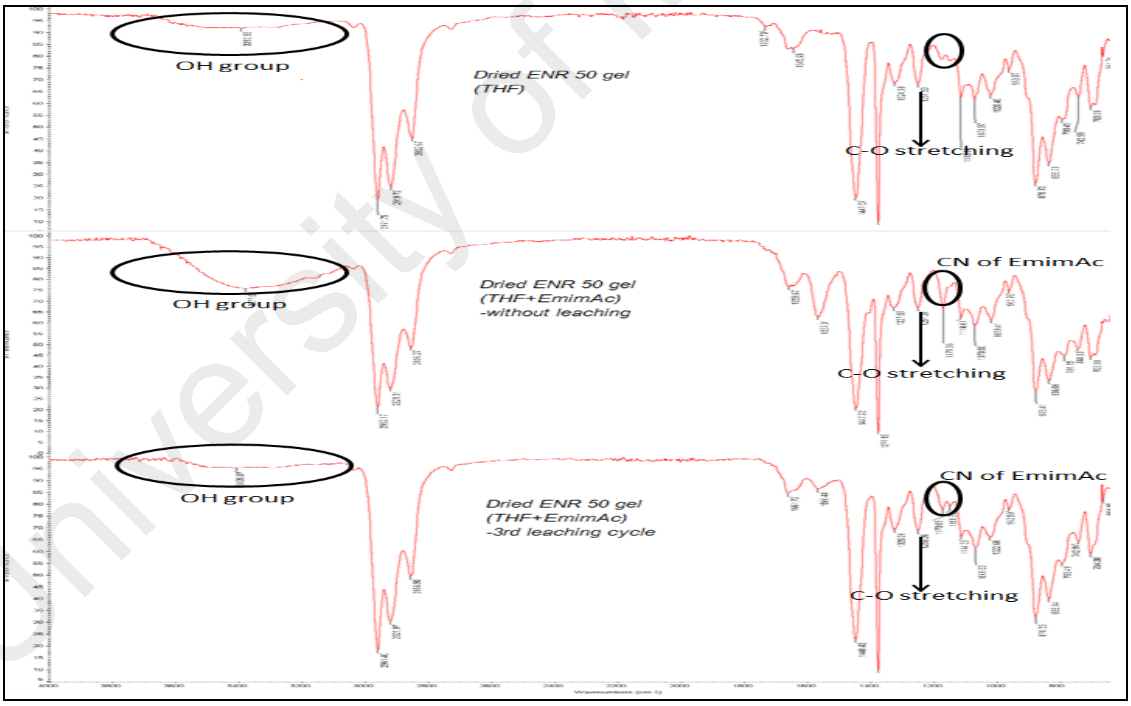

(b)

Figure 4.11 Increased peak intensity of OH and CN group for (a) Dried ENR 25 Gel (THF+EmimAc) and (b) Dried ENR 50 Gel (THF+EmimAc)

A broad OH peak from dried ENR 25 and ENR 50 gel (THF+BmimCl) with higher intensity than dried ENR 25 and ENR 50 gel (THF) was observed in the FTIR spectra.

It was confirmed by ^{1}H NMR where two additional peaks appeared at around 3.25 ppm and 3.82 ppm which were attributed to diol and furan respectively (Figure 4.12). These indicate species other than epoxide such as trans diol and furan have been produced as proposed in Scheme 1 and Scheme 2[4].

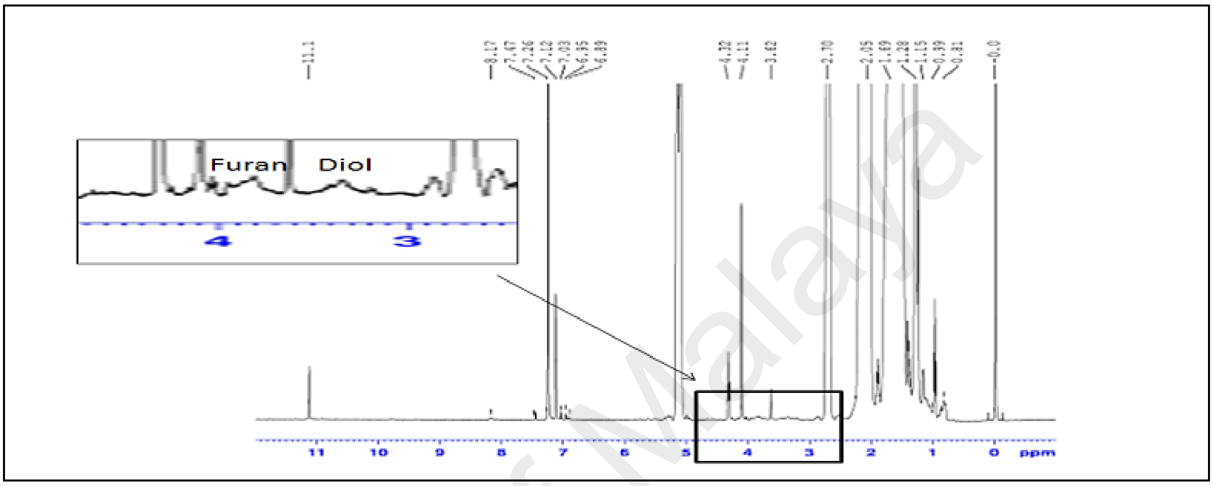

Figure 4.12 Ring opening peak in NMR spectrum

It was also observed that the leaching process was unable to completely remove the excess of IL where the peak associated to IL can still be seen in the NMR spectrum (e.g. EmimAc in Dried ENR 25 gel) as shown in Figure 4.13.

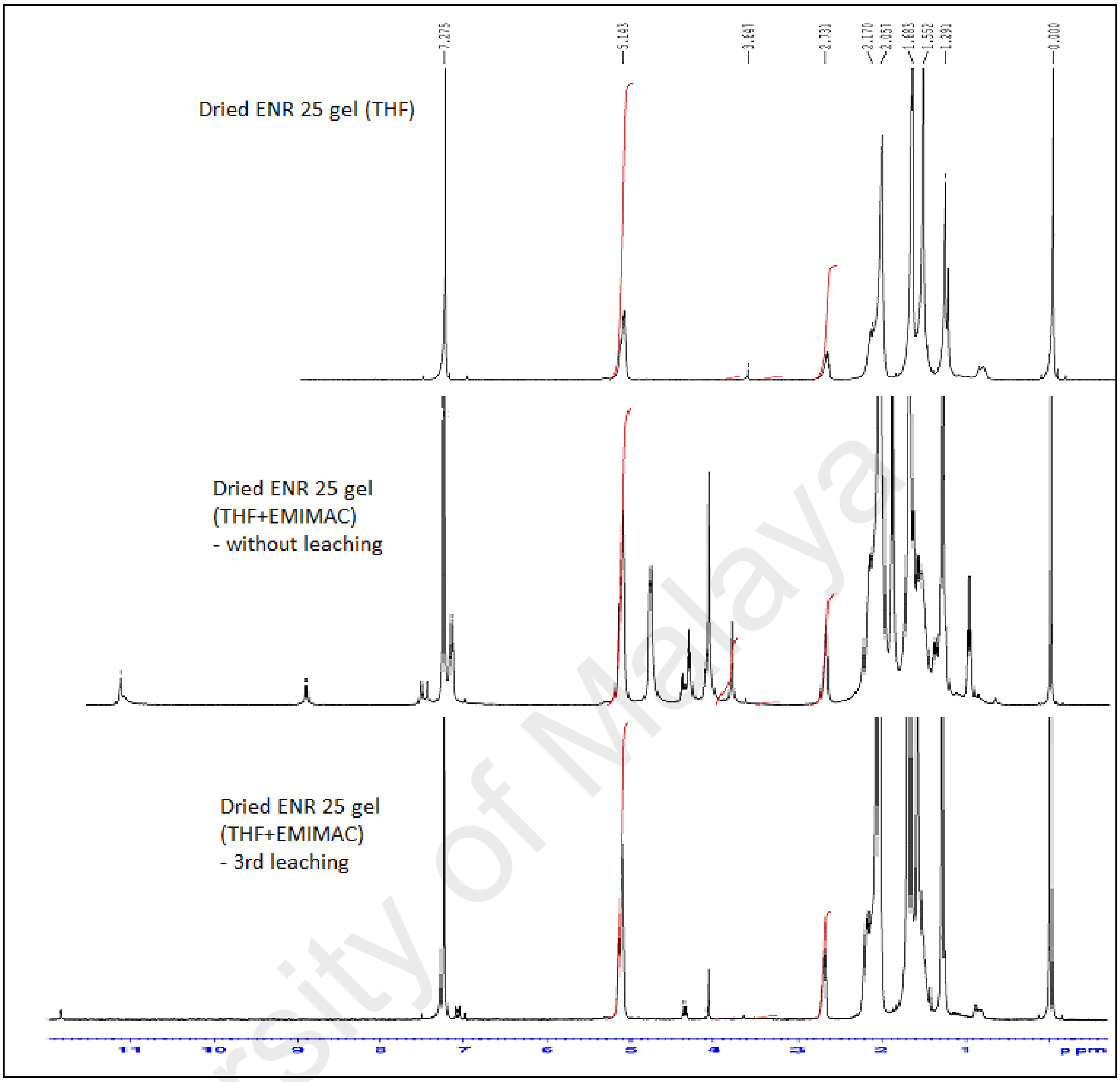

Figure 4.13 ^{1}H NMR spectrum of Dried ENR 25 gel (THF), Dried ENR 25 gel (THF+EmimAc) – without leaching and Dried ENR 25 gel (THF+EmimAc) – 3rd leaching

It was observed that the incorporation of BmimCl and EmimAc during gel content determinations were unable to reduce the gel content in ENR, however the ring opening products were observed as confirmed by FTIR and NMR analyses. We presume there were ring opening of epoxy groups occurred during the dissolution process that lead to the formation of ring opening products such as hydroxyl groups. But there is no obvious change on the intensity of absorption at around 1245 cm^{-1} corresponds to the C-O stretching of the epoxide ring (Figure 4.10 and Figure 4.11).

The possible dissolution mechanism of gel in IL is shown in Figure 4.14 and Figure 4.15. The $Bmim^+$ and Cl^- are expected to form bond with oxygen and hydrogen of the hydroxyl group. In the case of EmimAc, the Ac^- is expected to form bond with hydrogen. Complete dissolution process can only occur when the solute-solvent forces of attraction are great enough to overcome the solute-solute and solvent-solvent forces of attraction. At this point of analysis, the incomplete dissolution is might be due to the fact that the cations ($Bmim^+$ and $Emim^+$) and anions (Cl^- and Ac^-) are not enough to react with the entire epoxy groups which were attached to the backbone of ENR.

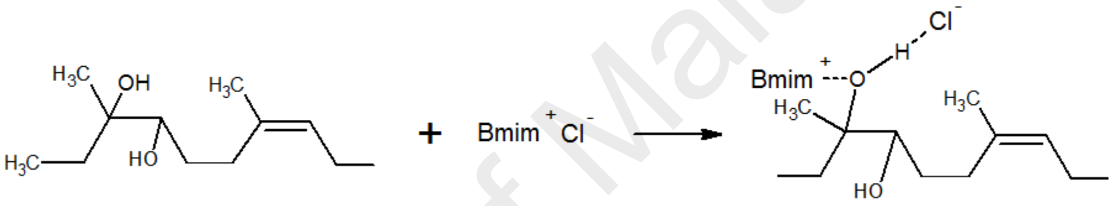

Figure 4.14 Possible dissolution mechanism of gel in BmimCl

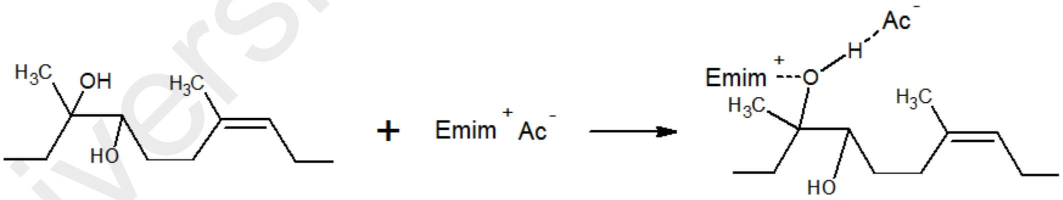

Figure 4.15 Possible dissolution mechanism of gel in EmimAc

The absence of heat during the process could be contributed to the incomplete dissolution of gel. In the dissolution of cellulose, cation and anion were separated at a certain temperature and able to form hydrogen bond with the cellulose and the solubility of cellulose can be increased up to 25 wt% with microwave heatings[26]. Therefore, introduction of heat during dissolution process may give greater impact, presumably solubilizing gel through hydrogen-bonding from hydroxyl functions to the anions of the solvent.

The purity of IL is another possibility that might cause failure in dissolving the gel. Both ILs were used directly without any treatment for removing water prior to gel content analysis. The presence of water in IL was shown to significantly decrease the solubility of cellulose through competitive hydrogen-bonding to the cellulose microfibrils, thus inhibits solubilization. Water content in IL at concentrations greater than ca. 1 wt% (approximately 0.5 mole fraction H_2O) significantly impaired the function of IL and eventually the cellulose was no longer soluble[22].

CHAPTER 5: CONCLUSION

Characterization of two grades of ENR namely ENR 50 and ENR 25 was successfully determined by FTIR, NMR and DSC. The observed characteristic peaks were consistent with those reported in previous works.

The used of different solvents (toluene, THF and chloroform) did not give any effect on the gel content values where both ENR 25 and ENR 50 exhibit high gel content regardless of types of solvent used. ENR 25 and ENR 50 which were soaked in the three different organic solvents demonstrated quite similar mean percentage of macro gel. The decreasing trend of cyclic ether absorption signal is due to the ring opening of the epoxy groups and lead to the formation of hydroxyl groups. A slight shift of T_g to higher temperature for the dried ENR 25 and ENR 50 gel as compared to the respective raw ENRs was observed. However, due to the ratio of ether crosslink present in the ENR is too little, the restriction in the molecular motion is undetectable by DSC.

Incomplete drying of the gel before the final weighing resulted in inconsistency in the gel measurement using Toluene+BmimCl. Hence, increasing trends were observed for the mean percentage of macro gel for both ENR 50 and ENR 25 with a large standard deviation recorded between replication. The gel content analysis was carried out using THF with the incorporation of BmimCl and EmimAc with the addition of leaching process before final weighing to leach out the excess IL. Slightly lower gel content values after the completion of third leaching cycle with a small standard deviation recorded between replication was obtained for SMR CV. This is a good indication that both ILs have potential in assisting the dissolution process. Increasing value of macro gel of ENR 25 (THF+BmimCl) as compared to ENR 25 (THF) was observed. There are no significant changes of the macro gel values of ENR 50 (THF+BmimCl) to compare with ENR 50 (THF). Both ENR 25 and ENR 50 which were dissolved in THF+EmimAc have showed lower macro gel values after the third leaching cycle. The macro gel value with large standard deviation between replication was obtained for ENR 50+THF+EmimAc due to inefficient leaching process.

It was observed that the incorporation of BmimCl and EmimAc during gel content determinations were unable to reduce the gel content in ENR, however the ring opening products such as hydroxyl and furan were observed as confirmed by FTIR and NMR analyses. We presume there were ring opening of epoxy groups occurred during the dissolution process that lead to the formation of ring opening products such as hydroxyl groups. But there is no obvious change on the intensity of absorption corresponds to the C-O stretching of the epoxide ring. At this point of analysis, the incomplete dissolution is might be due to the fact that the cations ($Bmim^+$ and $Emim^+$) and anions (Cl^- and Ac^-) are not enough to react with the entire epoxy groups which were attached to the backbone of ENR. The absence of heat during the process could be contributed to the incomplete dissolution of gel. Introduction of heat during dissolution process may give greater impact, presumably solubilizing gel through hydrogen-bonding from hydroxyl functions to the anions of the IL. The purity of IL is another possibility that might cause failure in dissolving the gel. Both ILs were used directly without any treatment for removing water prior to gel content analysis. The presence of water in IL could significantly decrease the solubility through competitive hydrogen-bonding.

FUTURE WORKS

In the current study, the ratio of IL to ENR was 1:0.5 (w/w) that has caused the incomplete dissolution. This could be due to the insufficient amount of cation and anion to react with the entire epoxy groups which were attached to the backbone of ENR. Therefore, the ratio can be optimized through a series of future work.

The absence of heat during the dissolution process leads to the incomplete dissolution of gel. Introduction of heat during dissolution process may give greater impact by solubilizing gel through hydrogen-bonding of hydroxyl functions from the ring opening of epoxy groups to the anions of the IL. The effect of various parameters such as temperature, soaking time and stirring can be carried out in the next attempt.

Meanwhile for the characterization, further work could be done with other instrumental techniques such as RAMAN spectroscopy to determine the changes in the unsaturation of the molecular structure of ENR, FESEM to study the morphological of the rubber gel and EDX to investigate the distribution of IL in the ENRs gel.

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