PREPARATION AND CHARACTERIZATION OF BLENDS OF POLY (ETHYLENE OXIDE) AND MONOCARBOXYLIC ACID MODIFIED EPOXIDIZED NATURAL RUBBER

WAN NURHIDAYAH BINTI A KARIM

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ABSTRACT

by reacting and a higher value has T_g value of In addition, t also This dissertation describes a study of using benzoic acid and acetic acid to fully ring-opened ENR50, which is natural rubber with 50% of the isoprene units epoxidized. ENR50 was chemically modified by ring opening the epoxide groups to produce a new chemically modified rubber. The reaction was carried out between the ENR50 dissolved in toluene with excess carboxylic acids (acetic acid and benzoic acid) at 105°C.Ring-opening of epoxide group by the carboxylic acids has led to an increase in the T_g due to the formation of polar –OH after ester groups, and the structural changes could be observed in the infra-red spectra (FTIR) and nuclear magnetic resonance (NMR). Changes in thermal properties were measured with thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC). The initial ENR50 has a $T_g$of -29ºC and the acetic acid modified sample (Ac-ENR50) has led to a new T_g of 20ºC while benzoic acid modified sample (Bz-ENR50) 12.3ºC.The effects of blend ratio of the modified rubber and poly(ethylene oxide) (PEO) in the presence of 2%dopantlithium perchlorate($LiClO_4$) were investigated. FTIR results showed that there was no reaction between the Ac-ENR50/PEO/$LiClO_4$ and Bz-ENR50/PEO/$LiClO_4$ blends. The Bz-ENR50/PEO/$LiClO_4$blends with the ratio at 30/70/2 have the highest value conductivity of 5.80X 10^{-7} S cm^{-1}. Morphologicalstudies of the blends were carried out by polarizing optical microscopy (POM) and results further confirmed the immiscibility of the two polymers. The spherulites could not be seen for the blends containing Bz-ENR50/PEO/$LiClO_4$higher than 50/50/2. Fibrillary fine texture of the spherulites of PEO was clearly observed at higher PEO content in the blends.

This dissertation describes a study of using benzoic acid and acetic acid to fully ring-opened ENR50, which is natural rubber with 50% of the isoprene units epoxidized. ENR50 was chemically modified by ring opening the epoxide groups to produce a new chemically modified rubber. The reaction was carried out between the ENR50 dissolved in toluene with excess carboxylic acids (acetic acid and benzoic acid) at 105°C.Ring-opening of epoxide group by the carboxylic acids has led to an increase in the T_g due to the formation of polar –OH after ester groups, and the structural changes could be observed in the infra-red spectra (FTIR) and nuclear magnetic resonance (NMR). Changes in thermal properties were measured with thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC). The initial ENR50 has a T_g of -29°C and the acetic acid modified sample (Ac-ENR50) has led to a new T_g of 20°C while benzoic acid modified sample (Bz-ENR50) 12.3°C.The effects of blend ratio of the modified rubber and poly(ethylene oxide) (PEO) in the presence of 2%dopantlithium perchlorate($LiClO_4$) were investigated. FTIR results showed that there was no reaction between the Ac-ENR50/PEO/$LiClO_4$ and Bz-ENR50/PEO/$LiClO_4$ blends. The Bz-ENR50/PEO/$LiClO_4$blends with the ratio at 30/70/2 have the highest value conductivity of 5.80X 10^{-7} S cm^{-1}. Morphologicalstudies of the blends were carried out by polarizing optical microscopy (POM) and results further confirmed the immiscibility of the two polymers. The spherulites could not be seen for the blends containing Bz-ENR50/PEO/$LiClO_4$higher than 50/50/2. Fibrillary fine texture of the spherulites of PEO was clearly observed at higher PEO content in the blends.

ABSTRAK

Disertasi ini menerangkan kajian penggunaan asid benzoik dan asid asetik untuk pembukaan gelang epoksi terhadap getah asli terepoksida yang mempunyai 50% tahap epoksida (ENR50) berbanding unit isoprena. ENR50 ini telah diubahsuaikan secara kimia dengan pembukaan gelang epoksi iaitu sebahagian dari kumpulan epoksida untuk menghasilkan getah yang diubahsuai secara kimia yang baru. Kajian dijalankan dengan melarutkan ENR50 ke dalam toluena dan bertindak balas dengan asid karbosilik (asid asetik dan asid benzoik) dalam kuantiti yang lebih banyak pada suhu 105°C. Pembukaan gelang epoksida yang disebabkan oleh asid karbosilik telah mendorong kenaikan suhu T_g apabila kehadiran kumpulan berfungsi –OH yang polar terhasil selepas kumpulan berfungsi ester, dan produk baru yang terhasil ini boleh dikaji dengan mengunakan spektroskopi jelmaan fourier infra merah (FTIR) dan spektroskopi resonans magnet nuclear (NMR). Perubahan ciri-ciri termal dikaji dengan menggunakan analisis termal gravimetrik (TGA) dan kalorimeter pengimbasan pembezaan (DSC). Untuk ENR50 yang tidak diubahsuai, suhu T_g adalah -29°C dan T_g bagi ENR50 yang telah diubahsuai dengan asid asetik (Ac-EN50) adalah 20°C sementara ENR50 yang telah diubahsuai dengan benzoik asid (Bz-ENR50) mempunyai nilai T_g iaitu 12.3°C. Selain itu, kesan daripada nisbah adunan antara ENR50 yang telah diubahsuai dengan asid asetik dan poli(etilena oksida) PEO yang didopkan dengan 2% jisim litium perklorat ($LiClO_4$) juga dikaji. Keputusan FTIR menunjukkan tiada tindak balas terhadap adunan Ac-ENR50/PEO/$LiClO_4$ dan Bz-ENR50/PEO/ $LiClO_4$. Adunan Bz-ENR50/PEO/$LiClO_4$ dengan nisbah 30/70/2 menunjukkan nilai kekonduksian elektrik paling tinggi iaitu 5.80 x 10^{-7} S cm^{-1}. Kajian morfologi dalam sistem campuran menggunakan mikroskop polarasi optik (POM) mengesahkan lagi ketidakserasian oleh dua kompenen adunan polimer. Jejari sferulit tidak dapat dilihat dengan jelas dalam adunan Bz-ENR50/PEO/$LiClO_4$ yang

mempunyai nilai lebih dari nisbah 50/50/2. Kadar pertumbuhan jejari sferulit PEO dapat dilihat dengan jelas pada nisbah PEO yang tinggi dalam adunan.

ABSTRACT

This dissertation describes a study of using benzoic acid and acetic acid to fully ring-opened ENR50, which is natural rubber with 50% of the isoprene units epoxidized. ENR50 was chemically modified by ring opening the epoxide groups to produce a new chemically modified rubber. The reaction was carried out between the ENR50 dissolved in toluene with excess carboxylic acids (acetic acid and benzoic acid) at 105°C. Ring-opening of epoxide group by the carboxylic acids has led to an increase in the T_g due to the formation of polar –OH after ester groups, and the structural changes could be observed in the infra-red spectra (FTIR) and nuclear magnetic resonance (NMR). Changes in thermal properties were measured with thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC). The initial ENR50 has a T_g of -29°C and the acetic acid modified sample (Ac-ENR50) has led to a new T_g of 20°C while benzoic acid modified sample (Bz-ENR50) 12.3°C. The effects of blend ratio of the modified rubber and poly(ethylene oxide) (PEO) in the presence of 2% dopant lithium perchlorate ($LiClO_4$) were investigated. FTIR results showed that there was no reaction between the Ac-ENR50/PEO/$LiClO_4$ and Bz-ENR50/PEO/$LiClO_4$ blends. The Bz-ENR50/PEO/$LiClO_4$ blends with the ratio at 30/70/2 have the highest value conductivity of 5.80 X 10^{-7} S cm^{-1}. Morphological studies of the blends were carried out by polarizing optical microscopy (POM) and results further confirmed the immiscibility of the two polymers. The spherulites could not be seen for the blends containing Bz-ENR50/PEO/$LiClO_4$ higher than 50/50/2. Fibrillary fine texture of the spherulites of PEO was clearly observed at higher PEO content in the blends.

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LIST OF ABBREVIATIONS AND SYMBOLS

$CDCl_3$	Deuterated chloroform
DPNR	Deproteinized Natural Rubber
DSC	Differential Scanning Calorimetry
EDPNR	Epoxidized Deproteinized Natural Rubber
ENR	Epoxidized Natural Rubber
ENR50	Natural rubber with 50 mol % epoxidation
FTIR	Fourier Transform Infrared Spectroscopy
HEDPNR	Hydrogenated Epoxidized Deproteinized Natural Rubber
K	Kelvin
$LiCIO_4$	Lithium perchlorate
NMR	Nuclear Magnetic Resonance Spectroscopy
PEO	Poly (ethylene oxide)
ppm	Parts per million
rpm	Revolution per minutes
SEM	Scanning Electron Microscope
T_c	Crystallization temperature
T_d	Temperature of Thermal degradation
T_g	Glass transition temperature
T_m	Melting temperature
TGA	Thermogravimetric Analysis
THF	Tetrahydrofuran

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CHAPTER 1 INTRODUCTION & LITERATURE REVIEW

1.1. Introduction

The term “Polymer” is derived from Greek: Poly meaning many and Meros meaning parts. Hence, “polymer” means a large molecule made up of many similar parts. Polymers are macromolecules that contained many repeated units, which are from the reactions of smaller molecules called monomers. They are widely found in our everyday life as materials in the human body, animals, plants, minerals and manufactured products. Proteins are carbohydrates are natural polymers in living organisms. Polyisoprene and resin are polymers from certain plants. Sand and stones are inorganic polymers. Various plastics such as polyethylene, polystyrene, PVC and nylon are some examples of synthetic polymers manufactured from petrochemicals.

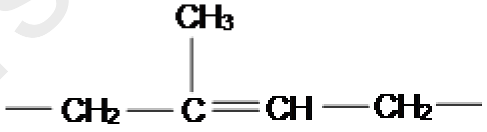
Chemical modifications of polymers are methods to change polymers through suitable chemical reactions, with the objectives to achieve certain desirable properties for the end-uses. Well known examples of such reactions include hydrogenation, chlorination grafting, degradation and crosslinking. Natural rubber, as first isolated from the rubber tree, is a weak material of not much use. Through crosslinking reactions with sulfur in a process known as vulcanization, it becomes a strong elastomer used in many products such as tyres and belts.

Beside chemical reaction, another important approach to modify polymers is the blending of a polymer with other materials. Blending of incompatible polymers is now a classical strategy to obtain a wide range of attractive properties for many applications and turns out to be one of the fastest growing branches of polymer technology. In particular, polymer electrolytes for applications in electronic and batteries could be produced from polymer blending. The combinations of an organic polymer and inorganic salt in polymer electrolyte (Chan et al., 2014) are now widely investigated as the basis of the electrolyte used in electrochemical devices such as displays, sensors, electrochromic windows, supercapacitors and rechargeable batteries. In particular there has been considerable interest regarding the use of polymer electrolyte system in solid polymer batteries (Glasse et al., 2002).

1.2. Epoxidized Natural Rubber

Natural rubber (NR) has been obtained from *Hevea brasiliensis* tree, which was originally found in South America. NR is a renewable and sustainable material, and gives various good properties, such as high tensile and elongation, and outstanding resilience, lending itself to be used in various applications.

NR is an unsaturated hydrocarbon that consists of mainly cis-1,4-polyisoprene as the repeating unit as shown in Figure 1.1.



$$-CH_2-\overset{\overset{\displaystyle CH_3}{|}}{C}=CH-CH_2-$$

Figure 1.1: Isoprene unit in natural rubber

Epoxidized natural rubber (ENR) is chemically modified form of NR. The epoxidation of NR in the latex form can be achieved using peracetic acid (Coomarasamy, 1981; Burfield et al., 1984) or performic acid (Ng & Gan, 1981; Geiling, 1984). In ENR, the NR molecular chains are being converted into the polar epoxy groups thus resulting in a decreasement in the free volume of chain and increases the density and polarity of the derivative. This provides the ENR with excellent air impermeability, oil and organic solvent proofness, wet road grip performance and so on (Yu et al., 2008). Epoxidation raises the glass transition temperature (T_g) by 0.93ºC for every mol% epoxidation (Gelling, 1985). In theory, any level of epoxidation can be achieved, but it is thought that only up to 50 mol% could be achieved in practice (Tanrattanakul et al., 2003).

1.3. Polyethylene oxide

PEO is a thermoplastic and a semi-crystalline synthetic polymer with chemical structure shown in Figure 1.2.

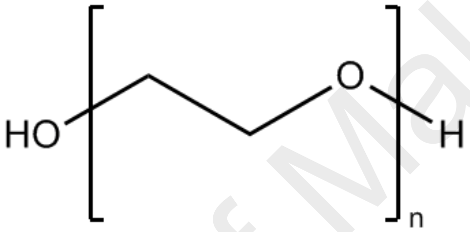


Figure 1.2: Chemical structure of poly(ethylene oxide)

PEO is nonionic, water-soluble with many applications due to its flocculent, thickening, sustained-release, lubrication, dispersing, and water-retention properties (Rodriguez, 1996). It can be synthesized by ring-opening polymerization of ethylene oxide with cationic, anionic or coordination initiators (Stevens, 1990). PEO is widely studied as conducting polymer electrolytes (Rodriguez, 1996) with potential application in battery.

Properties of PEO-based blends are strongly influenced by blend compositions, crystallinity, thermal behavior and morphologies (Zhong & Guo, 2000; Chan et al., 2011; Pereira et al., 2011). The glass transition temperature (T_g) of PEO is -67ºC and melting temperature (T_m) is 65ºC (Chrissopoulou et al., 2011). A convenient and effective method to improve PEO film properties is by blending PEO with other polymers (Zivanovic et al., 2007).

1.4. Blends of PEO and ENR

The blending of two or more polymers has been important technique to create new materials with different physical properties, and may result in improving the cost performance, savings in time and energy as compared to the efforts to invent a totally new material (Cowie, 1973; Kienzle, 1988; Haldar et al., 1998). Mixing of polymers may produce miscible and immiscible blends. Miscible blend results in an average of the properties and have fewer issues of appearance, properties and rheology due to existence of strong intermolecular forces. On the other hand, immiscible blend may combine the favorable characteristics of each component and produce very useful properties (Seong, 1998; Feng et al., 2015).

The situation might become more challenging when there are chemical interactions between the functional groups of different polymers. Thus the reactions involving epoxies in ENR and functional groups of another polymer have led to the development of self crosslinkable blends. These include the blend of chlorosulfonated polyethylene rubber CSM/ENR, carboxylic-acrylonitrile-butadiene rubber XNBR/ENR (Alex et al., 1989), polychloroprene CR/ENR, CR/XNBR/ENR and CSM/XNBR/ENR (Roychoudhury et al., 1992) that formed crosslinked networks upon heating at elevated temperature. ENR and alkyd could also form self crosslinkable blend in toluene solution at ambient temperature. The crosslinking reactions between the epoxide groups of ENR and –COOH groups of alkyd has formed ester linkages with subsequent increase in T_g and gel content of the blend (Khong & Gan, 2013).

PEO has shown miscibility with poly(vinyl alcohol) (Sotele et al., 1997), poly(n-butyl methacrylate)(PBMA) (Shafee & Ueda, 2002) and poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) (PHBV) (Tan et al., 2006) via intermolecular interactions but forming immiscible blend with poly(ε-caprolactone) (PCL) (Qiu et al., 2003) and ENR (Chan & Kammer, 2008). Thermal properties of blends of PEO and ENR had been reported (Chan et al., 2011) to be immiscible in all proportions, as shown by the existence of two T_gs in DSC analysis.

Immiscible polymer blends could have other advantages. Combination of crystalline and amorphous polymer may show good dimensional stability, ease of processing, chemical resistance and mechanical properties for specific application (Cimmino et al., 1990). Polymer blends containing ENR with 50% epoxide level (ENR-50) and polyhydroxybutyrate (PHB) exhibit reaction involving carboxyl end of PHB and epoxide group of ENR (Lee et al., 2005).

ENR is compatible with poly(vinyl chloride) (PVC) (Varughese et al., 1988) and poly(methyl methacrylate) (PMMA) (Nakason et al., 2004) but immiscible with PHBV (ChanIsmail et al., 2004) and poly(ethylene terephthalate) (PET) (Sulaiman et al., 2009).

One important area for polymer blending is in developing polymer electrolyte application. PEO-based polymer electrolytes of poly(propylene oxide) (PPO)/PEO (Morales et al., 1996), poly(methyl vinyl ether-maleic acid) (PMVE-MAc)/PEO/lithium perchlorate ($LiClO_4$) (Rocco et al., 2002), poly(bisphenol A-co-epichlorohydrin) (PBE)/PEO/$LiClO_4$ (Rocco et al., 2004) and PEO/NR/lithium benzenesulfonate (LiBs) (Yoshizawa et al., 2000) have been extensively studied. ENR/lithium triflate ($LiCF_3SO_3$) is studied as ENR-based polymer electrolyte (Idris et al., 2001). PEO/ENR/$LiClO_4$ (Chan

& Kammer, 2008; Sim et al., 2010) ENR/PEO/$LiCF_3SO_3$ (Glasse et al., 2002) and PEO/ENR50/$LiCF_3SO_3$ (Noor et al., 2009; Noor et al., 2010) have been studied as conducting polymer systems.

Miscibility and morphology of semicrystalline/semicrystalline (ChanKummerlöwe et al., 2004; Chan & Kammer, 2008) and semicrystalline/amorphous (Chee et al., 2005) polymer blends have been extensively studied in recent years. Most polymers are immiscible with PEO, that is, the polymer blend forms a heterogeneous system (Chan & Kammer, 2008).

Chan and Kammer (2008) who had carried out a study on properties of solid solutions of PEO/Epoxidized natural rubber blends and $LiClO_4$ observed that the immiscible blending of the polymer system corresponds to the presence of two glass transition temperatures. Values of T_gs of both polymers increase with the addition of $LiClO_4$. The increase in T_gs is approximately constant over the entire range of blend composition. The degree of crystallinity of PEO in blends with ENR descends only to a minor extent with ascending ENR content. Incorporation of the salt to the blend significantly suppresses the rate of crystallization of PEO in the blend.

(Sulaiman et al., 2009) studied the thermal properties and morphologies of PET in blends with ENR of 25 and 50 mol% of epoxy content, ENR25 and ENR50 respectively. It has been observed that the blend in the system is immicible as there are two T_gs which are correspond to the neat constituent. The degree of crystallinity of PET in blends with ENR25 remains constant while increase in blend between PET and ENR50. Rate of crystallisation of PET in the blends decreases exponentially as the T_c increase.

Dispersed phases of ENR25 and ENR50 in the matrix of PET also can be observed when the content of PET is in excess.

1.5. Chemical modification of ENR

ENR can be represented by the following structure, where each molecule has epoxy and unsaturated sites. Figure 1.3 shows a chemical structure of modified NR with 50 mol% epoxidation (ENR50).

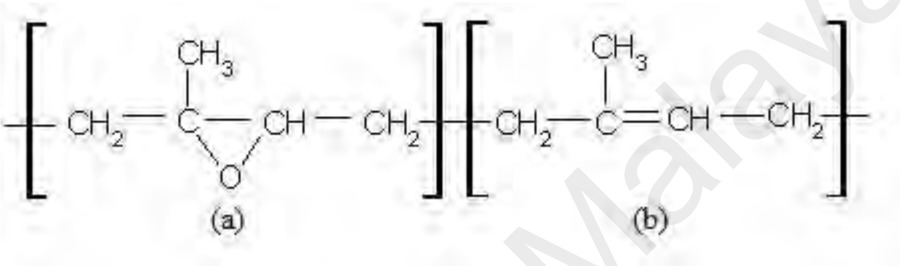


Figure 1.3: Chemical structure of ENR50 with (a) epoxy and (b) unsaturated sites.

The double bonds in ENR can be crosslinked by sulphur and peroxide, whereas the epoxy groups provide alternative sites for reactions with compounds having other functional groups (Loo, 1985; Baker et al., 1986; Gan & Burfield, 1989; Varughese & Tripathy, 1992; Hashim & Kohjiya, 1994). Thus ENR could be crosslinked through the reaction with carboxylic acids, amine compounds or aminosilanes (Akiba & Hashim, 1997).

In latex stage, hydroxyl group has been introduced to deproteinized natural rubber (DPNR) by using peracetic acid. Hydrogenation of epoxidized deproteinized natural rubber (EDPNR) was then performed with p-toluenesulfonylhydrazide (PTSH) in p-xylene at 135^{o}C to produce hydrogenated epoxidized natural rubber (HENR) (Nghia et al., 2008). In HENR, epoxy groups that are randomly distributed into isoprene units and epoxy groups are converted to hydroxyl groups after hydrogenation as shown in Figure 1.4.

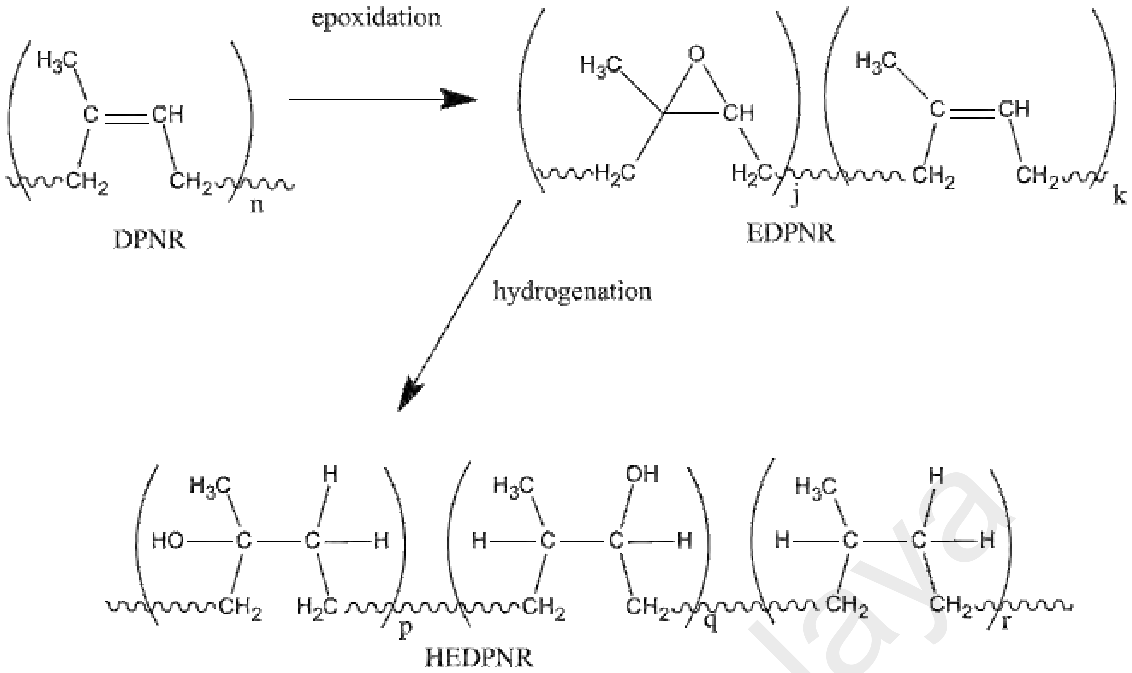


Figure 1.4: Hydrogenation of HEDPNR (Nghia et al., 2008)

In this study (Nghia et al., 2008) ^{1}HNMR spectra analysis provided the clear characteristic between DPNR, EDPNR and HEDPNR. For DPNR, three signals characteristic of methyl, methylene and unsaturated methane protons of *cis*-1,4-isoprene units appeared at 1.68, 2.05 and 5.1ppm respectively. For EDPNR two signals appeared at 1.29 and 2.7 ppm which were assigned to methyl and methane protons and resulting epoxy group. The intensity ratio of the signals can be estimated using Equation (1) where I is the intensity of the signals and the subscripts numbers represent the chemical shift value.

$$Xepoxy = \frac{I_{2.7}}{I_{2.7} + I_{5.1}} x\ 100 \qquad (1)$$

After hydrogenation of EDPNR with *p*-toluenesulfonylhydrazide, new signals appear around 0.8-1.8 and 3.4 ppm whereas the signals of 2.7 and 5.1 ppm disappear. The residual double bond is estimated using Equation (2).

$$Xresidual\ double\ bond = \frac{I_{5.1}}{(I_{5.1} + I_{0.8})/3} x\ 100 \qquad (2)$$

Crosslinking of ENR with dibasic acids was investigated by previous researcher (Loo, 1985). The crosslinking of ENR with these dibasic acids takes place via ring opening of the epoxide. The formation of diester linkage is shown in Figure 1.5 using oxalic acid. In this study various dibasic acids were used to crosslink with the ENR. In the IR spectra analysis for the vulcanized sample the carbonyl band of 1680-90 cm^{-1} of the unvulcanized sample shifted to 1710 cm^{-1}. These confirmed the conversion of the carbonyl group of the dibasic acid to the ester groups as crosslinks were formed. The diacid vulcanizates of ENR50 were found to have very low compression set and resilience with increasing state of crosslinking.

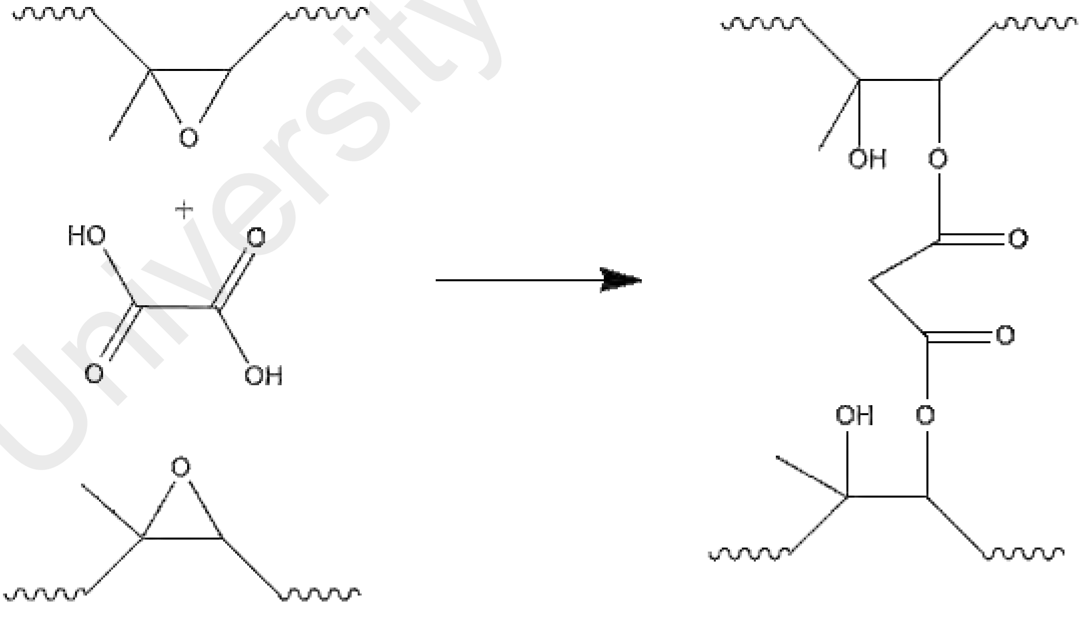


Figure 1.5: Crosslinking of ENR with oxalic acid (diacid) with subsequent formation of a diester linkage (Loo, 1985)

The epoxide groups from ENR also can be ring opened by amino acids at the latex stage to give a functionalized rubber with short carboxylic side-chains or zwitterion form as shown in Figure 1.6. During the storage of dry rubber, crosslinks could form by condensation reactions with alcohol (Gan, 1997).

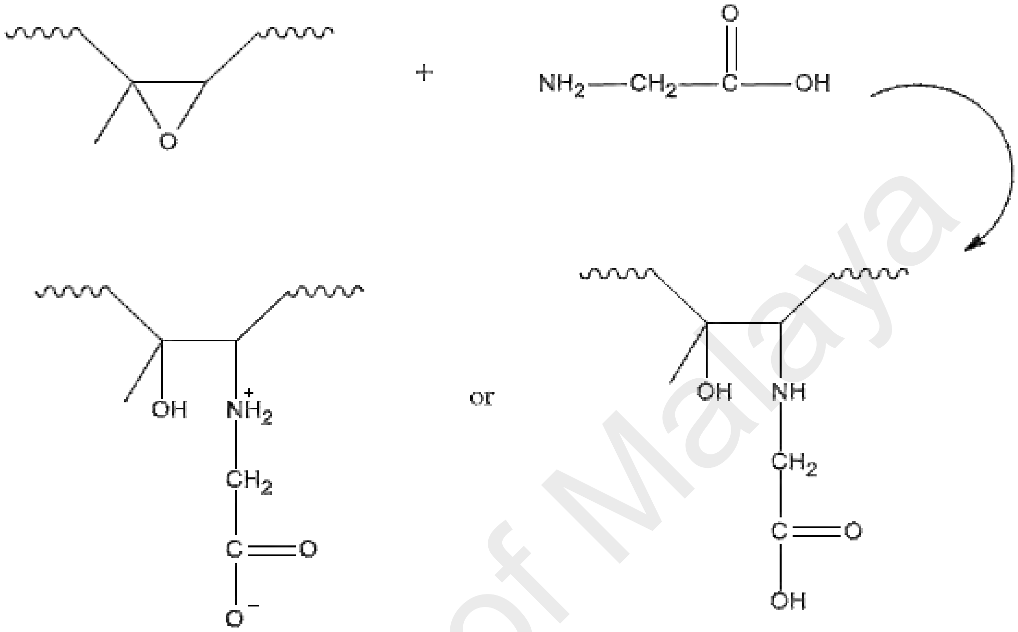


Figure 1.6: Epoxide ring opening by amino acids at the latex stage (Gan, 1997)

The other technique of chemical modification of ENR is by grafting with amine compounds (Hashim & Kohjiya, 1994). This reaction involved ring opening of the epoxy groups. It has been shown that ENR-amine curing reaction has higher activation energy and high T_g. This is due to the bulkiness of the amine crosslinks and hydrogen bonding effect. Figure 1.7 shows the grafting reaction involving the ring opening of the epoxy groups.

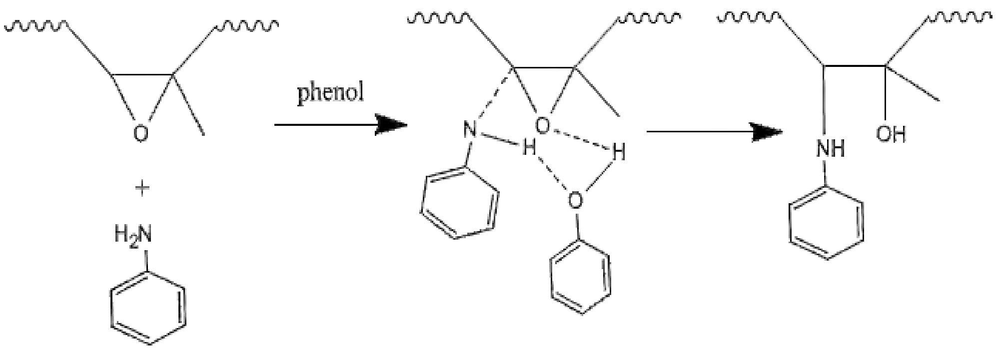


Figure 1.7: Phenol catalysed grafting reaction of ENR with aniline (Hashim & Kohjiya, 1994)

The reactions between ENR and benzoic acid as shown in Figure 1.8 have been investigated at elevated temperatures in the range 125-160°C. A significant increase in T_g of the material, whereby the increase was proportional to the amount of incorporated benzoic acid was obtained. The presence of the polar hydroxyl group, has introduced the possibility of inter and intramolecular hydrogen bondings and activation energy was approximately 70 $kJmol^{-1}$ (Gan & Burfield, 1989).

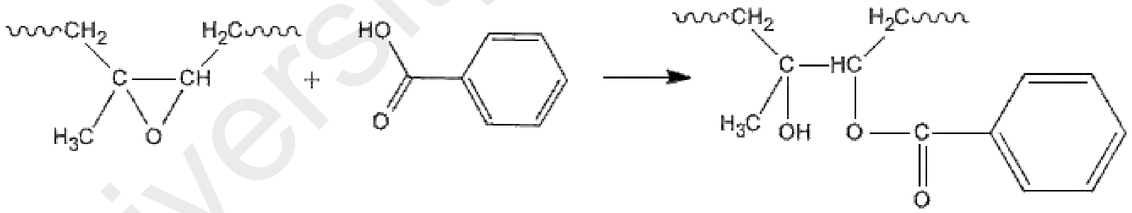


Figure 1.8: A plausible reaction between ENR and benzoic acid. (Gan & Burfield, 1989)

Gan and Hamid (Gan & Hamid, 1997) had shown that the chemical modification of ENR with conversion of epoxide groups to diols can be achieved by reacting ENR50 with water and acetic acid in tetrahydrofuran at 60°C as shown in Figure 1.9. Under this condition the partial ring-opening of ENR50 by hydrolysis of the epoxide groups has resulted in higher level of diols as calculated from ^{1}HNMR spectra.

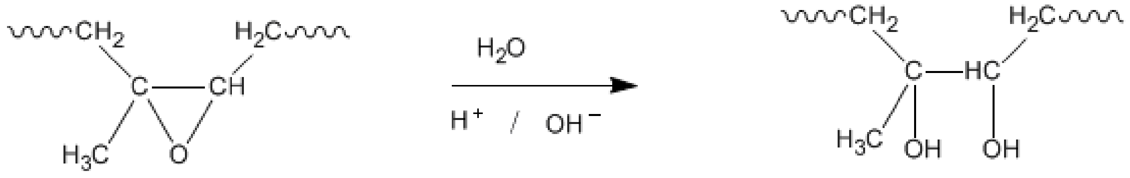


Figure 1.9: A plausible reaction between ENR50 with water and acetic acid in THF

1.6. Problem Statement

ENR50 contains both epoxide and unsaturated sites. The epoxide groups serve as the site for further chemical modification through its reactions with other reactive groups. In this project, ENR50 was treated with an excess of mono-carboxylic acid to ring-open all the epoxide groups. The reaction was carried out between ENR50 dissolved in toluene with each of acetic and benzoic acids at 105°C. As expected, the introduced polar groups have increased the intermolecular interaction leading to higher T_g. These modified rubbers are then blended with PEO at different ratios, with lithium salt added as dopant, and the new materials are characterized. This research study is important to investigate the compatibility of Bz-ENR50/PEO/$LiClO_4$ blends. This blend gives a potential application as solid polymer electrolyte which serves as membrane separator in lithium-ion battery for hybrid vehicles.

1.7. Significance of Study

The success of this project may lead to a fundamental understanding of the modification of ENR to form carboxylic acid-modified ENR50 that leads to higher polarity compared to ENR50 which probably has more coordination sites for lithium cation salvation and will result in improved conductivity.

1.8. Objective of Study

The main aim of this study was to prepare higher polarity of ENR50 through the modification with carboxylic acid that lead to more coordination sites for lithium cation salvation and result in improved conductivity.

Other specific objectives of the research were to:

i. synthesize Ac-ENR and characterize this modified rubber.
ii. synthesize Bz-ENR50 and characterize this modified rubber.
iii. compare between physical and chemical properties of ENR50, Ac-ENR50 and Bz-ENR50.
iv. investigate on the miscibility of Bz-ENR50/PEO/$LiClO_4$ blends.
v. investigate the morphologies of Bz-ENR50/PEO/$LiClO_4$ blends.
vi. measure the conductivity measurements on Bz-ENR50/PEO/$LiClO_4$ blends

1.9. Scope of Study

1) Preparation of Ac-ENR50 and Bz-ENR50
2) Purification of Ac-ENR50 and Bz-ENR50
3) The characterization parameters investigated in preparation of ENR50 with carboxylic acid are:

    i. Fourier Transform Infrared Spectroscopy
    ii. ^{1}H NMR Spectroscopy
    iii. Thermal Gravimetric Analysis
    iv. Differential Scanning Calorimetry

4) Preparation of the blends Bz-ENR50/PEO/$LiClO_4$ by solution casting method using different ratios of 100/0/2, 90/10/2, 80/20/2, 70/30/2, 60/40/2, 50/50/2, 40/60/2, 30/70/2, 20/80/2, 10/90/2 and 0/100/2.

5) The characterization parameters investigated in the blends are:
    i. Conductivity
    ii. Polarizing Optical Microscopy
    iii. Fourier Transform Infrared Spectroscopy

CHAPTER 2 EXPERIMENTAL

2.1 Materials and reagents

ENR50 was provided by Malaysia Rubber Board (MRB) (Sungai Buloh, Malaysia) and used as supplied. PEO (Mη = 1x10^5 g mol^{-1}) was purchased from Sigma-Aldrich Co. Lithium perchlorate with 99% purity was obtained from Across Organic Company (Geel, Belgium). Commercially available chemicals such as toluene, chloroform, benzoic acid and glacial acetic acid were supplied by Merck (Darmstadt, Germany) and methanol was obtained from Bumi-Pharma Sdn Bhd (Malaysia).

2.2 Preparation of Ac-ENR50 and Bz-ENR50

In order to prepare Ac-ENR50, 90 g of ENR50 was mechanically masticated on a laboratory two-rolls mill at room temperature for forty passes. The sample was then cut into small pieces with a pair scissors, before it was placed into a one-liter round bottom reaction flask that was equipped with mechanical stirrer, water condenser and a dropping funnel. 450 mL of toluene was added into the reaction flask and stirred at 150 rpm until the ENR50 has dissolved. The heating mantle was turned on and the solution was slowly heated until the temperature reached 105°C. Then, 120 mL of glacial acetic acid was added through a dropping funnel, as shown in Figure 2.1. The speed of the stirrer was maintained around 200 rpm. To monitor the progress of the reaction, 10 mL of the reaction mixture was taken at the specified reaction times, and the rubber was isolated by precipitation method using excess methanol.

Figure 2.1: The set-up of modification Ac-ENR50.

Reaction was carried out for 24 h and the content in the flask was mixed with excess of methanol which is five times more than the original amount of sample. This procedure is to precipitate the modified ENR50, which was then isolated by filtration. The filtrate that contained excess unreacted acetic acid was discarded; the isolated rubber was washed with fresh methanol before being dried in vacuum oven at 50^{o}C for 24 h. Samples were stored in desiccators. On the other hand, to prepare Bz-ENR50, the similar procedure which has been described previously was used, except that the acetic acid was changed to benzoic acid. Table 2.1 presents the properties of Ac-ENR50 and Bz-ENR50.

Table 2.1: Properties of Ac-ENR50 and Bz-ENR50.

Properties	**Ac-ENR50**	**Bz-ENR50**
Carboxylic acid	glacial acetic acid	benzoic acid
Colour	light brownish	dark brownish

2.3 Purification of Ac-ENR50 and Bz-ENR50

20 g of the dried Ac-ENR50 was cut into smaller pieces and dissolved in 500 g of chloroform in a conical flask. Teflon coated magnetic stirrer was added to the conical flask and the polymer solution was placed on hot plate stirrer (IKA 9008100, Staufen, Germany) with stirring speed of 300 rpm at 50°C for 24 h.

Then, the solution was filtered using nylon cloth to remove gel content. The filtered polymer solution was placed on hot plate stirrer at 50°C with stirring speed of 200 rpm to condense the solution by removing the solvent. The final viscous solution was poured slowly into a big beaker containing methanol and the solution was kept stirring until gel-like precipitate formed. The ratio of polymer solution to methanol was 1:5.

The purified Ac-ENR50 was placed on Teflon dish and left overnight in fume hood to evaporate off excess solvent. Sample was dried in oven at 50°C for 24 h and further dried in vacuum oven for another 24 h at 50°C. Samples were stored in desiccators after drying for further analyses. The same procedure was repeated for the other Bz-ENR50 sample.

2.4 Preparation of the blends

Bz-ENR50/$LiClO_4$, PEO/$LiClO_4$ and Bz-ENR50/PEO/$LiClO_4$ were prepared by using a solution casting method. The modified ENR50 and PEO were separately dissolved in a chloroform to form 5% (w/w) solutions. The solutions with 2% $LiClO_4$ salts in each of the components were mixed and stirred continuously for 24 h to ensure homogeneous mixing. Thin films of the blends were prepared by casting the homogenized solution mixture in Teflon dishes. Chloroform was allowed to evaporate off by left the sample overnight in the fume hood at room temperature. Thin films of polymers were further dried in vacuum oven at 50°C for another 24 h to ensure they were free of solvent. The thin films obtained were stored in desiccators before further analyses. Table 2.2 shows the variation of sample prepared with different Bz-ENR50 to PEO ratios.

Table 2.2: Sample prepared with different blending ratio.

Weight of Bz-ENR50 (g)	Weight of PEO (g)	Weight of $LiClO_4$ (g)	Ratio Bz-ENR50/PEO
1.20	0.00	0.024	100/0
1.08	0.12	0.024	90/10
0.96	0.24	0.024	80/20
0.84	0.36	0.024	70/30
0.72	0.48	0.024	60/40
0.60	0.60	0.024	50/50
0.48	0.72	0.024	40/60
0.36	0.84	0.024	30/70
0.24	0.96	0.024	20/80
0.12	1.08	0.024	10/90
0.00	1.2	0.024	0/100

2.5 Characterization for the Modified ENR50

2.5.1 Fourier Transform Infrared Spectroscopy

Fourier Transform Infrared Spectroscopy (FTIR) is a technique which is used to identify types of chemical bonds (functional groups) in a molecule. FTIR is an effective analytical instrument for detecting functional groups and characterizing covalent bonding information.

A thin layer of the sample dissolved in minimum amount of toluene was coated directly onto the sodium chloride cell and the solvent was removed under reduced pressure in a vacuum oven at 50°C to deposit a thin polymer film on the sodium chloride cell. FTIR spectra of the polymer films were recorded using a Perkin Elmer Spectrum 400 (Waltham, Massachusetts, USA) FTIR instrument. FTIR spectra were recorded in the transmittance mode over the range of 450 - 4000 cm^{-1} at a resolution of 4 cm^{-1}.

2.5.2 ^{1}H NMR Spectroscopy

^{1}H Nuclear Magnetic Resonance spectroscopy were recorded on JNM-GSX 270 MHz Fourier transform NMR spectrometer (Peabody, Massachusetts, USA). 0.2 g of sample was dissolved in 5 mL of $CDCl_3$ with tetramethylsilane (TMS) as internal standard.

2.5.3 Thermal gravimetric analysis

Perkin Elmer TGA 6 (Norwalk, Connecticut, USA) was used to investigate the thermal stability by heating 10 mg of the sample from 50°C to 600°C at a heating rate of 10°C min^{-1} under nitrogen atmosphere. Onset temperature, T_d, is the onset of the weight loss.

2.5.4 Differential Scanning Calorimetry

In this work glass transition temperature (T_g), melting temperature (T_m), and melting enthalpy (ΔH_m) were determined using TA DSC Q200 (New Castle, Delaware, USA) equipped with cooling system (RCS 90, New Castle, Delaware, USA). The DSC was calibrated with indium standard under nitrogen atmosphere. About 6 to 10 mg of sample was encapsulated in an aluminium sample pan. For isothermal crystallization determination, blends of Ac-ENR50 were held at 80°C for 5 min followed by cooling to 49°C at a cooling rate of 20°C min^{-1} and allowed to crystallize. Afterwards, samples were heated to 80°C at a heating rate of 10°C min^{-1}. For T_g analysis, the same procedure as mentioned above is used, except the samples were cooled to -70°C and held for 1 min.

2.6 Characterization of polymer blends (Bz-ENR50/$LiClO_4$, PEO/$LiClO_4$ and Bz-ENR50/PEO/$LiClO_4$ blends)

2.6.1 Conductivity

The ionic conductivities of the films were measured using Hioki 3532-50 LCR Hi-Tested together with a computer for data acquisition over the frequency range between of 50 Hz to 1 MHz at room temperature. The films were sandwiched between two stainless steel disc electrodes, which serve as blocking electrodes for the ions. The ionic conductivity of the sample can be calculated by using the R_b value as in the Equation (3).

$$\sigma = \frac{t}{R_b \; x \; A} \tag{3}$$

where t is the thickness of the film, R_b is bulk impedance and A is the film-electrode contact area. Film thickness was measured using Mitutoyo Digimatic Caliper (Model: ID-C1012XBS). The average of thickness, L, was calculated from three measurements of thickness on the polymer film at different positions that were in contact with stainless steel disk electrodes.

2.6.2 Polarizing Optical Microscopy

Morphologies of the growing spherulites in Bz-ENR50/PEO blends were studied using Olympus Microscopes and Imaging Analysis Software systems (Olympus BX51). The microscope was equipped with a heating/cooling unit (Mettler Toledo, FP90). The sample was heated from 30°C to 80°C at 10°C min^{-1}. It was annealed at 80°C for 1 min followed by cooling to 39°C at a cooling rate 20°C min^{-1}. During isothermal crystallization at 39°C, micrographs were captured at suitable time intervals ranging from 1 to 15 s. Measurement of diameter of the growing spherulites were carried out by using Cellsens Standard software. For morphology determination of sample after isothermal crystallization, heating and cooling cycles were applied as before and micrograph was taken after 1 hour of crystallization at 39°C.

CHAPTER 3 RESULTS AND DISCUSSION

3.1. Characterization of ENR50, Ac-ENR50 and Bz-ENR50

3.1.1. Fourier Transform Infrared (FTIR) Spectroscopy

Ring-opening reaction of the epoxide group by carboxylic acid has been reported by a number of earlier papers (Hayashi et al., 1981, Gan and Burfield, 1989, Lee et al., 2011). A plausible reaction of the epoxide group with acetic acid and benzoic acid are illustrated in Figure 3.1.

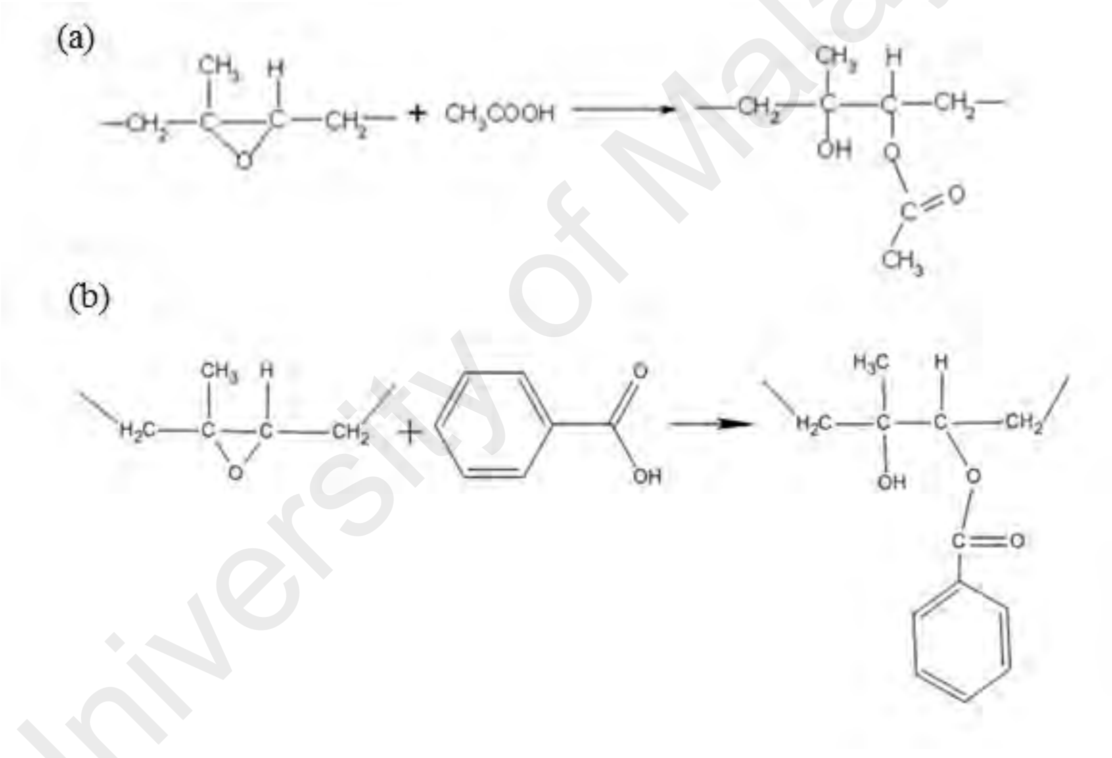


Figure 3.1: A plausible reaction of the epoxide group with (a) acetic acid (b) benzoic acid.

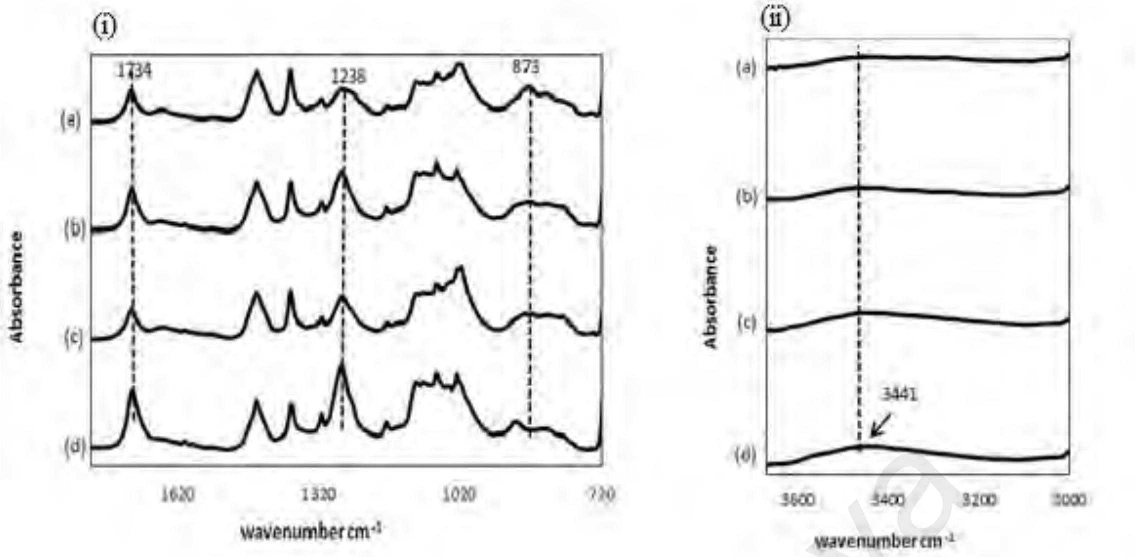


Figure 3.2: FTIR spectra in the region of (i) 720-1800 cm^{-1} and (ii) 3000-3600 cm^{-1} for (a) ENR50, and Ac-ENR50 at various reaction times (b) 10 h (c) 18 h and (d) 24 h

Figure 3.2 shows the FTIR spectra in the region of 720-1800 cm^{-1} and 3000-3600 cm^{-1} for ENR50 and Ac-ENR50 at various reaction times of 10 h, 18 h and 24 h. Ring opening of epoxide group by acetic acid produced hydroxyl group as shown by the broad band at 3441 cm^{-1}. This absorbance band became more intensified as a function of reaction time. The strong stretching at 1734 cm^{-1} and 1238 cm^{-1} gradually increased with the reaction time indicating the formation of C=O and C-O bond in ester. The other parts of the spectra, particularly the peak at 873 cm^{-1} corresponds to the epoxide groups gradually decreased as reaction time was increased indicating the epoxide groups were ring-opened.

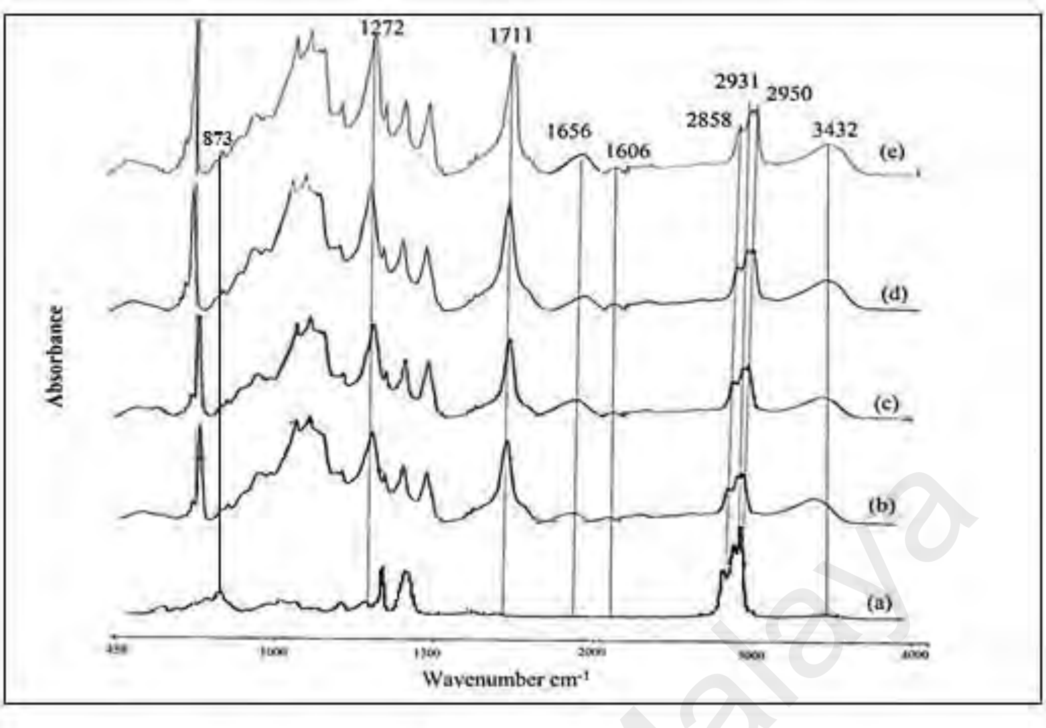


Figure 3.3: FTIR spectra of (a) ENR50 and Bz-ENR50 at various reaction times (b) 5 h (c) 7 h (d) 14 h and (e) 24 h

The FTIR spectrum of 24 h Bz-ENR50 in Figure 3.3 shows the disappearance of peak at 873 cm^{-1} indicating that the ring from the epoxide groups has opened. As the reaction time increased, the absorbance gradually decreased. Peaks at 1606 cm^{-1} clearly indicates that aromatic ring pattern is gradually increased as the reaction time increased. The broad peak at 3432 cm^{-1} is due to hydroxyl group (Gan & Hamid, 1997). The strong peak at 1711 cm^{-1} resulting from the carboxyl group C=O group which have been grafted onto ENR50. The strong stretching peak at 1272 cm^{-1} gradually increased with the reaction time indicating the presence of C-O bond in the ester linkage. These results further proved that the esterification process and formation of hydroxyl group had occurred with a decrement of epoxy groups.

FTIR is a very powerful tool for investigating specific interactions in synthesizing polymer. There are two types of hydrogen bonding that exist in this polymeric system which are intermolecular and intramolecular hydrogen bonding amongst polymer chains (Khan & Poh, 2011). In FTIR spectrum for Ac-ENR50 and Bz-ENR50 (24 h), a broad band was observed in the region of 3441 cm^{-1} which is correspond to the –OH group which indicates there are intramolecular and intermolecular hydrogen bonds that exist in this polymeric system (Riyajan, 2014). The possible intermolecular hydrogen bonding is shown in Figure 3.4 (Teik, 1988).

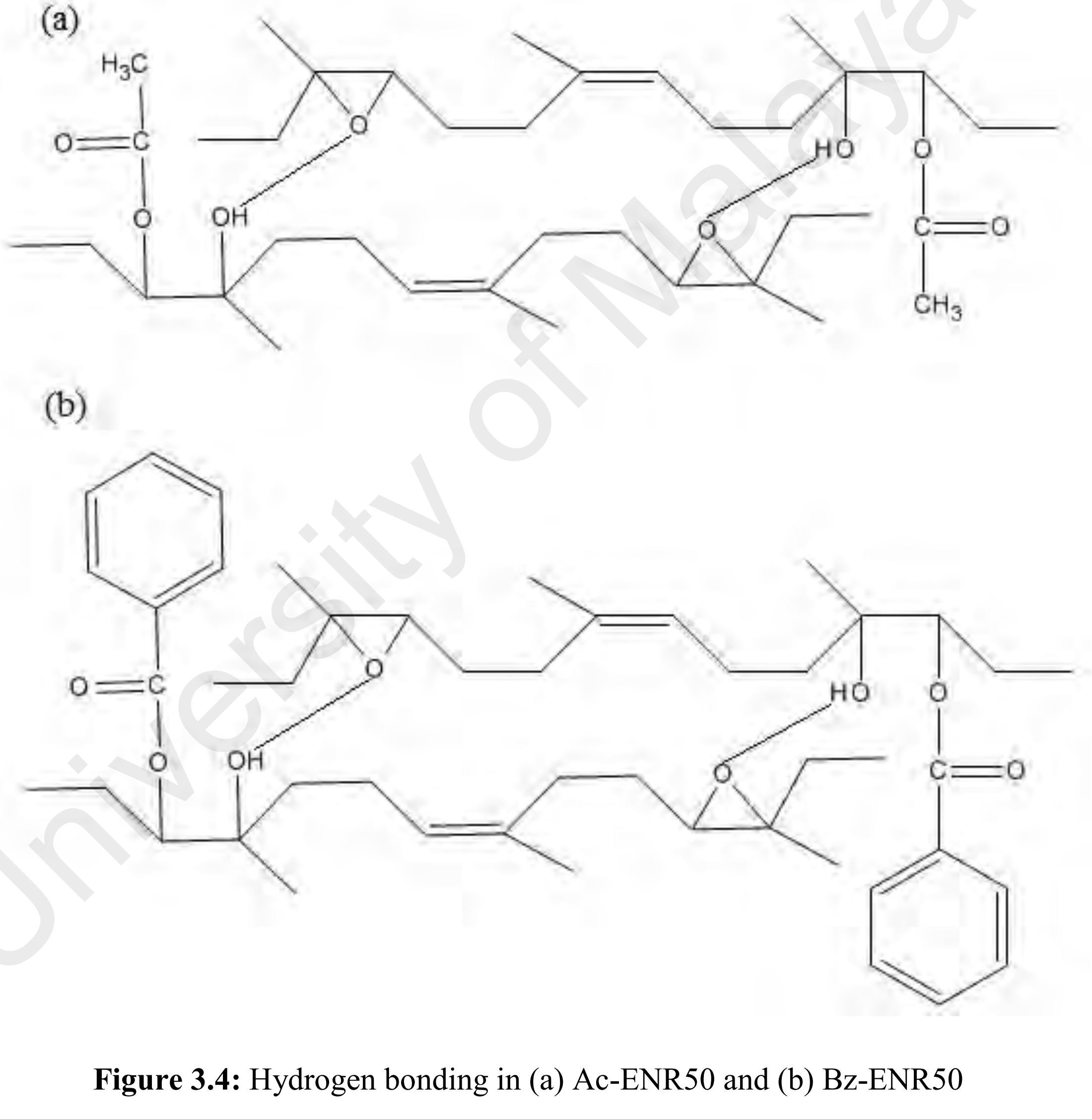


Figure 3.4: Hydrogen bonding in (a) Ac-ENR50 and (b) Bz-ENR50

Figure 3.5 shows the FTIR spectra for ENR50 before and after modification. The characteristic bands of saturated aliphatic C-H bonds in ENR50 before modification are observed at 2965, 2931 and 2858 cm^{-1} which corresponds to the C-H stretching, while 1452 and 1378 are correspond to CH_2 scissoring and CH_2 wagging, respectively. On the other hand, C=C stretching band is related to the peak observed at 1656 cm^{-1}. Meanwhile, the peak of epoxide group is seen at 873 cm^{-1}. Table 3.1 shows the band characteristics for ENR50 before the modification.

Table 3.1: Wavenumbers and assignments of IR bands exhibited by ENR50

Wavenumber (cm^{-1})	Assignment	Functional group	References
2965	CH_2 asymmetric stretching	Methylene	(Bunce et al., 1993; Arjunan et al., 2001; Van Zyl et al., 2003; Zong-Qiang et al., 2008)
2931	CH_2 asymmetric stretching	Methylene	(Arjunan et al., 2001; Van Zyl et al., 2003; Zong-Qiang et al., 2008)
2858	CH_2 asymmetric stretching	Methylene	(Arjunan et al., 2001; Van Zyl et al., 2003; Zong-Qiang et al., 2008)
1656	C=C streching	Olefin	(Smith, 1999; Ali et al., 2008; Peng et al., 2016)
1452	CH_2 scissoring	Alkene	(Smith, 1999)
1378	CH_2 wagging and methylene	Alkene	(Smith, 1999; Arjunan et al., 2001)
873	C-O stretching (hydrofuran ring)(5-ring ether)	Epoxy	(Davey & Loadman, 1984; Van Zyl et al., 2003)

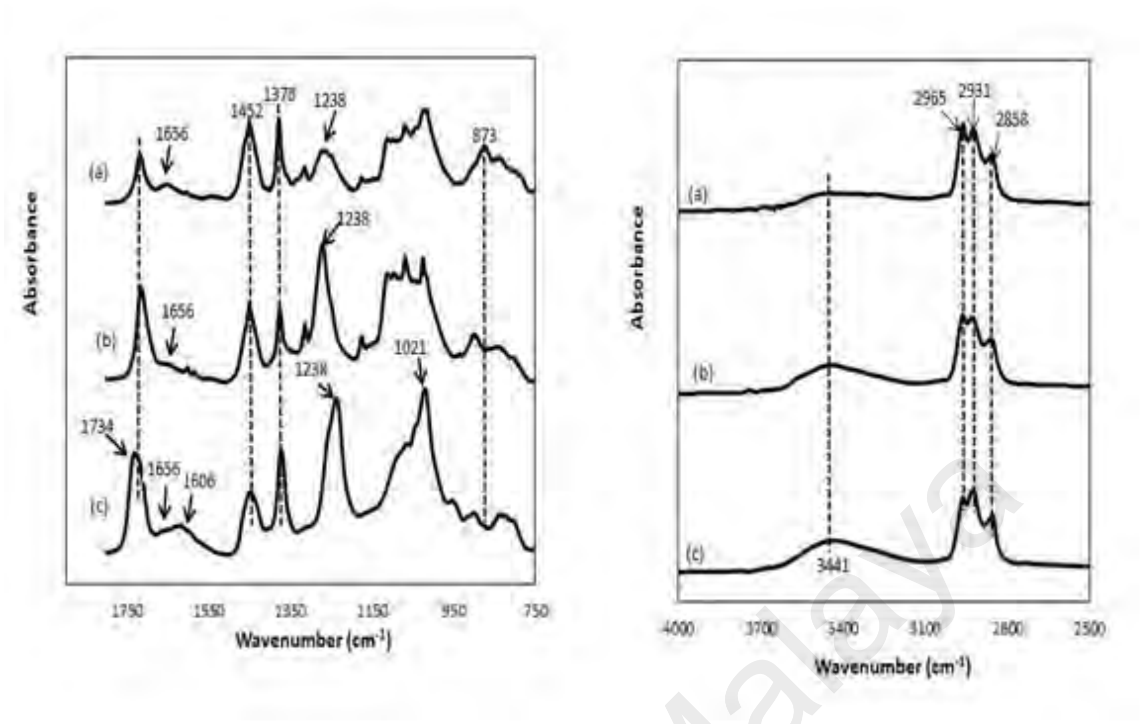


Figure 3.5: Absorbance FTIR spectra of (a) ENR50 (b) Ac-ENR50 and (c) Bz-ENR50.

For the Ac-ENR50 and Bz-ENR50 after 24 h of reaction, the broad absorption in the region 3441 cm^{-1} is due to the hydroxyl functional –OH stretching. The characteristic bands of saturated aliphatic C-H stretching are observed at 2965, 2931 and 2858 cm^{-1}. The band for –CH_2- scissoring is located at 1452 cm^{-1}. The band for -C–CH_3 is located at 1378 cm^{-1}, the strong peaks at both 1238 cm $^{-1}$ and 1734 cm^{-1} indicate the presence of C-O, while C-O-C stretching at 1021 cm^{-1}. The disappearance of peak at 873 cm^{-1} indicates that the epoxide rings for Ac-ENR50 and Bz-ENR50 have been opened. The C=C stretching band is located at 1656 cm^{-1} and peak at 1606 cm^{-1} indicates that the aromatic ring in Bz-ENR50. The characteristics absorption peaks for Ac-ENR50 and Bz-ENR50 are listed in Table 3.2 and Table 3.3.

Table 3.2: Wavenumbers and assignments of IR bands exhibited by Ac-ENR50

Wavenumber (cm^{-1})	Assignment	Functional group	References
3441	-OH streching	Hydroxyl	(Gelling, 1988)
2965	CH_2 asymmetric stretching	Methylene	(Arjunan et al., 2001; Van Zyl et al., 2003; Zong-Qiang et al., 2008)
2931	CH_2 asymmetric stretching	Methylene	(Arjunan et al., 2001; Van Zyl et al., 2003; Zong-Qiang et al., 2008)
2858	CH_2 asymmetric stretching	Methylene	(Arjunan et al., 2001; Van Zyl et al., 2003; Zong-Qiang et al., 2008)
1734	C=O stretching for ester	Ester	(Gan & Hamid, 1997; Sin et al., 2010)
1656	C=C streching	Olefin	(Smith, 1999; Ali et al., 2008; Peng et al., 2016)
1452	CH_2 scissoring	Alkene	(Smith, 1999)
1378	CH_2 wagging and methylene	Alkene	(Smith, 1999; Arjunan et al., 2001)
1238	C-O stretching for ester	Ester	(Davey & Loadman, 1984; Loo, 1985; Ali et al., 2008)
1021	C-O-C stretching for ester	Ester	(Loo, 1985; Mohanty et al., 1996; Van Zyl et al., 2003; Ali et al., 2008)
873	C-O stretching (hydrofuran ring)(5-ring ether)	Epoxy	(Davey & Loadman, 1984; Van Zyl et al., 2003)

Table 3.3: Wavenumbers and assignments of IR bands exhibited by Bz-ENR50

Wavenumber (cm^{-1})	Assignment	Functional group	References
3441	-OH streching	Hydroxyl	(Gelling, 1988)
2965	CH_2 asymmetric stretching	Methylene	(Arjunan et al., 2001; Van Zyl et al., 2003; Zong-Qiang et al., 2008)
2931	CH_2 asymmetric stretching	Methylene	(Arjunan et al., 2001; Van Zyl et al., 2003; Zong-Qiang et al., 2008)

2858	CH_2 asymmetric stretching	Methylene	(Arjunan et al., 2001; Van Zyl et al., 2003; Zong-Qiang et al., 2008)
1734	C=O stretching for ester	Ester	(Gan & Hamid, 1997; Sin et al., 2010)
1606	Aromatic =C-H bending	Aromatic ring	(Xue, 1997; Khan & Poh, 2011; Lievens et al., 2011; Obinaju et al., 2014)
1656	C=C streching	Olefin	(Smith, 1999; Ali et al., 2008; Peng et al., 2016)
1452	CH_2 scissoring	Alkene	(Smith, 1999)
1378	CH_2 wagging and methylene	Alkene	(Smith, 1999; Arjunan et al., 2001)
1238	C-O stretching for ester	Ester	(Davey & Loadman, 1984; Loo, 1985; Ali et al., 2008)
1021	C-O-C stretching for ester	Ester	(Loo, 1985; Mohanty et al., 1996; Van Zyl et al., 2003; Ali et al., 2008)
873	C-O stretching (hydrofuran ring)(5-ring ether)	Epoxy	(Davey & Loadman, 1984; Van Zyl et al., 2003)

3.1.2. ^{1}H NMR Spectroscopy

^{1}H NMR spectroscopy was carried out to verify the chemical structure of ENR50 and investigate the possible chemical structure of Ac-ENR50 and Bz-ENR50. The degree of epoxidation of ENR50, Ac-ENR50 and Bz-ENR50 was estimated from intensity ratio of the signals at 5.1 and 2.7 ppm. These signals which are assigned to the olefinic and epoxy methane protons were used for calculating the epoxy content of the polymer in mol by following Equation (4). The degree of conversion of epoxide group, E is given by Equation (4), in which

$$E = \frac{xep(0) - xep(t)}{xep(0)} \tag{4}$$

where xep (0) is mol% of epoxide groups in control ENR50 *xep* (t) is mol% of epoxide group content at reaction time (t)

Table 3.4: Epoxide content (%) and degree of conversion of epoxide group at various reaction times for Ac-ENR50 and Bz-ENR50.

Reaction time (h)	**Epoxide content (%) in Ac-ENR50**	**Degree of conversion, *E* for Ac-ENR50**	**Epoxide content (%) in Bz-ENR50**	**Degree of conversion, *E* for Bz-ENR50**
Control	52.4	0	52.4	0
3	-	-	37.9	0.28
5	-	-	32.4	0.38
7	-	-	29.6	0.44
10	32.0	0.39	-	-
14	-	-	23.7	0.55
18	24.8	0.53	-	-
24	16.0	0.69	9.91	0.81

The mol epoxide content (%) is gradually decreased with the reaction time. The epoxy group was converted to hydroxyl and ester; –OH of the hydroxyl was at 4.6 ppm. The ester $–COOCH_3$ of Ac-ENR50 was seen at 4.0 ppm. In the case of Bz-ENR50, the aromatic protons appeared around 7.2–7.5 ppm (Liu et al., 2014) Table 3.4 shows the mol epoxide content (%) and degree of conversion of epoxide group at various reaction times in (h) for Ac-ENR50 and Bz-ENR50.

Figure 3.6 summarizes the ^{1}HNMR spectra for (a) ENR50 (b) Ac-ENR50 and (c) Bz-ENR50 at 24 h of reaction. At 24 h reaction time, 16% and 9.91% of epoxide groups were left in Ac-ENR50 and Bz-ENR50 respectively. The degree of conversion to hydroxyl and ester increased for both carboxylic acid-modified ENR50.

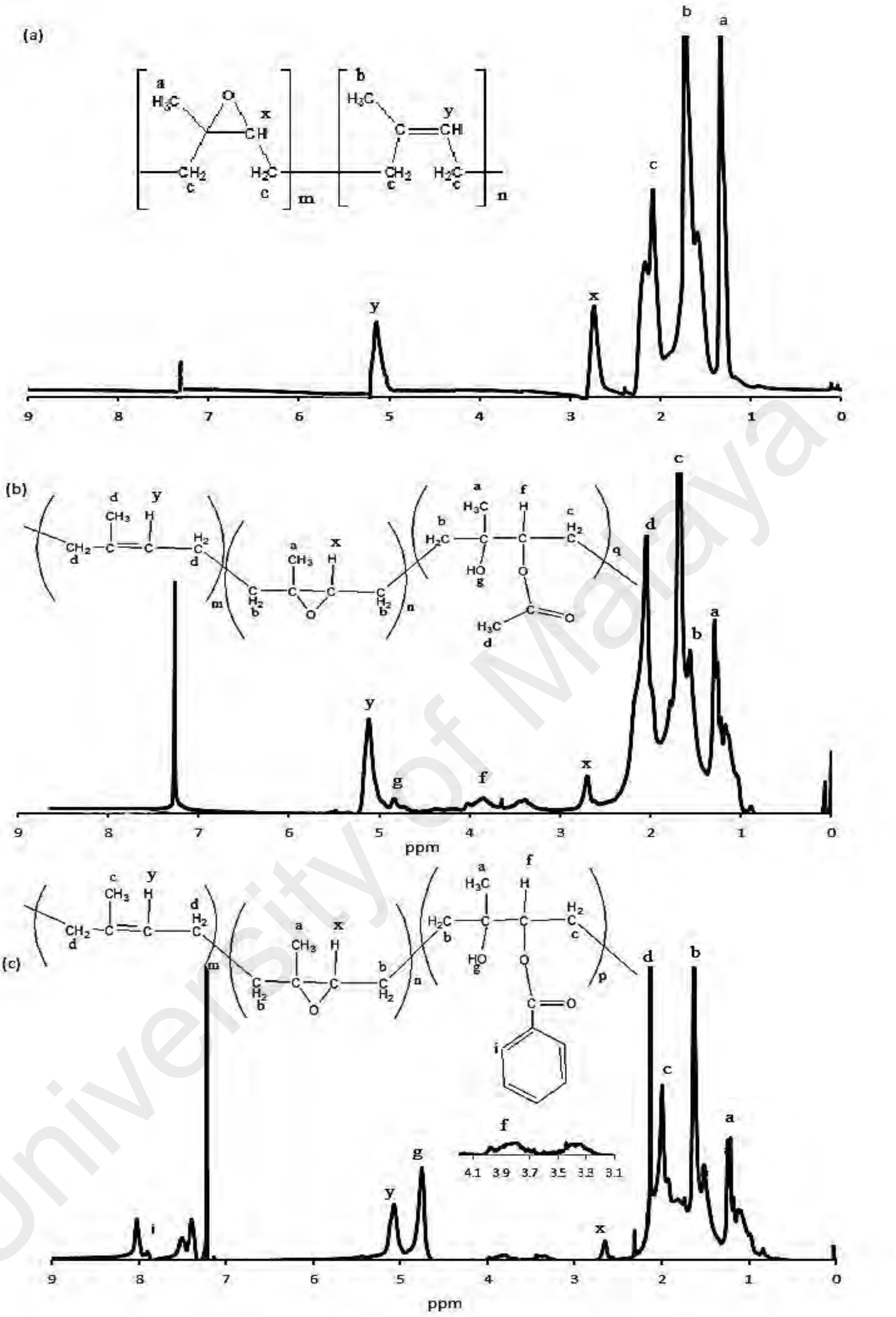


Figure 3.6: ^{1}HNMR spectra for (a) ENR50 (b) Ac-ENR50 and (c) Bz-ENR50

3.1.3. Thermogravimetric Analysis (TGA)

TGA has been performed in a nitrogen atmosphere was performed. There was no noticeable weight loss before the T_d, consistent with the fact that the sample was free of solvent. For the initial ENR50 sample, the thermal degradation occured in one-step decomposition from 320-550ºC, whereas for the Ac-ENR50 samples at reaction time of 15 h and 24 h, four-step thermal decomposition were observed. The first degradation of about 10% weight loss was within 100-220ºC for 15 h sample and within 120-280°C for 24 h sample. This degradation could be due to the acetate groups breaking away as acetic acid. The second step was observed at 220-320ºC for 15 h and at 280-350ºC for 24 h with approximately 13% of weight loss and this could be attributed to the loss of –OH with accompanying dehydration (Intharapat et al., 2016). These two minor degradations might generate unsaturation which allowed a crosslink process to be occurred. The major loss occurred at third step in the temperature range of 320-510ºC for 15 h and 350-500ºC for 24 h with weight loss around 65% relating to the decomposition of the rubber backbone chains. The final step was around 510-656ºC for 15 h and 500-664ºC for 24 h with weight loss about 8% corresponding to the carbon decomposition.

Three degradation steps were seen in 7 h and 24 h Bz-ENR50. The first degradation occurred between 220-305ºC for 7 h and 250-330ºC for 24 h with weight loss of 15% and it could be attributed to the loss of –OH with accompanying dehydration (Intharapat et al., 2016). The second degradation was around 305-480ºC for 7 h and 330-440ºC for 24 h corresponding to the major weight loss of about 80%. The third degradation was seen around 480-580ºC for 7 h and 440-580ºC for 24 h corresponding to about 5% weight loss corresponding to the carbon decomposition. Figure 3.7 shows TGA and DTG curves of ENR50, Ac-ENR50 for 24 h and Bz-ENR50 for 24 h.

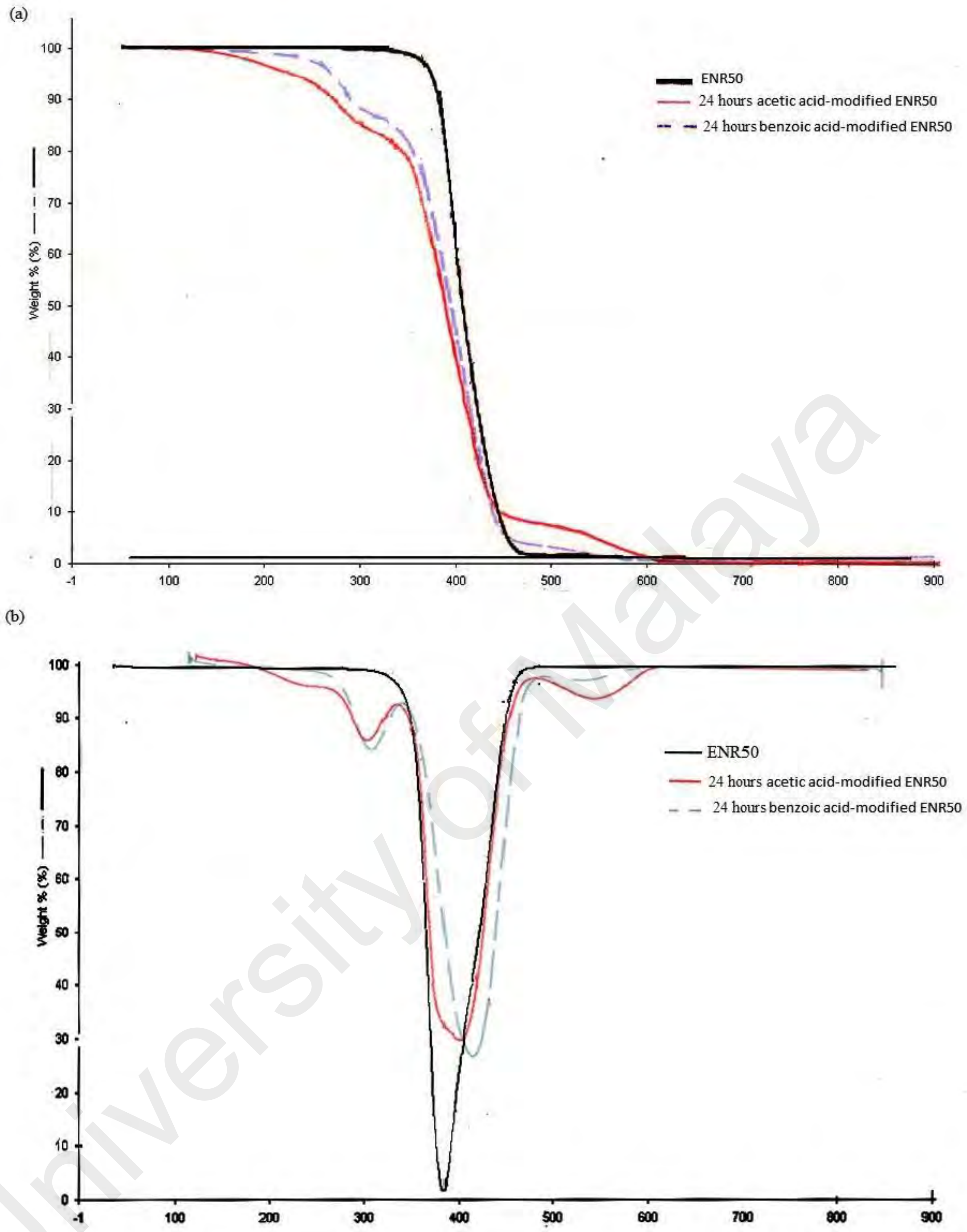


Figure 3.7: TGA and DTG curves of ENR50, 24 hours Ac-ENR50 and 24 hours Bz-ENR50.

To obtain thermodynamic parameters by Kissinger equation, the relationship between heating rates and temperature at most rapid degradation is tabulated in Table 3.5 and the graph of $-\ln(q/T^2_p)$ versus $1/T_p$ is shown in Figure 3.8. (Sin et al., 2010)

Table 3.5: Thermodynamic parameters for thermal degradation of Ac-ENR50 for 24 hours reaction time

Reaction time (hour)	q (/K min^{-1})	T_p (/K)	$1/T_p$ (x10^{-3} K)	-ln (q/T^2_p)	E$_a$, Activation energy (kJ^{-1}mol)	A Pre-exponential factor (x 10^3 s^{-1})
24	5	632.7	1.58	11.29	82.6	1007.24
	10	643.1	1.55	10.63		
	15	664.9	1.50	10.29		
	20	685.8	1.46	10.07		
	25	682.3	1.47	9.83		

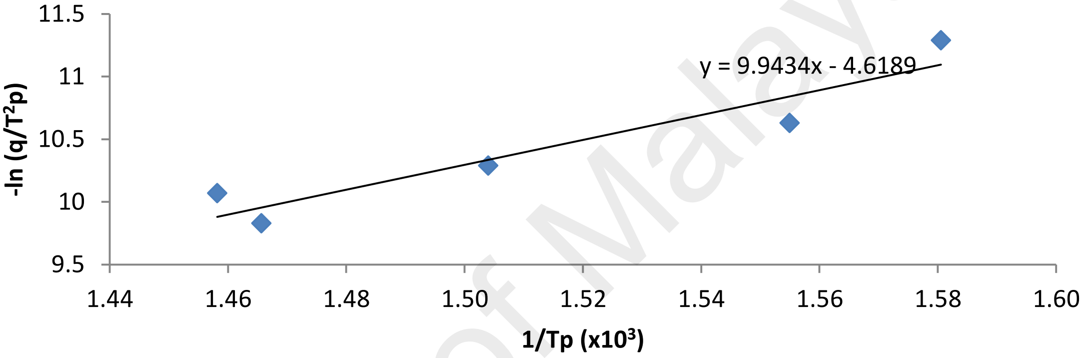


Figure 3.8: Graph of –ln(q/T^2_p) versus $1/T_p$ for 24 hours Ac-ENR50

The degradation activation energy and pre-exponential factor of the process were estimated using Kissinger equation as shown in Equation (5).

$$-\ln\left(\frac{q}{T^2p}\right) = \frac{E_d}{RT} - \ln(AR/E_d) \qquad (5)$$

Where

q = heating rate (K min $^{-1}$)

T_p = maximum degradation temperature (K)

R = universal gas constant (8.314 J K^{-1}mol^{-1})

E_d = degradation activation energy (J mol^{-1})

A = pre-exponential factor (s^{-1})

From the linear plot of $-\ln(q/T^2_p)$ versus $1/T_p$, activation energy and pre-exponential factor could be calculated from the slope and the intersection at y-axis respectively (Sin et al., 2010). The entropy of activation (ΔS) for 24 hours Ac-ENR50 thermal degradation was also calculated following Equation (6).

$$A = \left(\frac{kT_p}{h}\right) e^{\Delta S/R} \tag{6}$$

Where

A = Arrhenius parameter (s^{-1})

k = Boltzman constant

T_p = peak temperature (K)

h = Plank constant (Js)

ΔS = entropy of activation (J $K^{-1}mol^{-1}$)

R = universal gas constant (8.314 J $K^{-1}mol^{-1}$)

Taking into account the relationship between activation energy E_a, ΔH can be determined using Equation (7).

$$E_a = \Delta H + nRT \tag{7}$$

Finally using Equation (7) the value for ΔH and using the Gibbs-Helmholtz thermodynamic relationship (Marinović-Cincović et al., 2013) in Equation (8) , ΔG of the activated complex formation from the reagents can be calculated.

$$\Delta G = \Delta H - T\Delta S \tag{8}$$

The degradation activation energy, E_a and pre-exponential factor, A for 24 hours Ac-ENR50 were 82.6 kJ mol^{-1} and 1007.24 x 10^3 s^{-1} respectively. Table 3.6 also shows the change of activation entropy (ΔS) has a negative value for 24 hours, i.e. -136.4 J^{-1} K mol^{-1}, and that the relatively high E_a indicates that thermal degradation can only occur at high temperature.

Table 3.6: The values of entropy of activation, enthalpy of activation and Gibbs free energy activation for the main degradation steps.

Reaction time (hour)	ΔS (J^{-1} K mol^{-1})	ΔH (kJ mol^{-1})	ΔG (kJ mol^{-1})
24	-136.4	820.74	907.04

According to the results, during drying for 24 hours of Ac-ENR50, the positive enthalpy change ($\Delta H>0$) responds to sensible heat and requires energy in order to promote changes, which is usually observed during drying process. The positive value for Gibbs free energy of activation ($\Delta G>0$) means that the phenomenon is not spontaneous and actually requires energy from the environment so that the process can occur (Marinović-Cincović et al., 2013).

3.1.4. Differential Scanning Calorimetry (DSC)

Table 3.7 show all the DSC data for Ac-ENR50 samples with different reaction times. T_g of ENR50 was measured at -29.00°C. Chemical modification by carboxylic acid has increased the T_g value to 20.03°C and 12.25°C, for Ac-ENR50 and Bz-ENR50, respectively. The corresponding increase in T_g from the modification of ENR50 by benzoic acid has been discussed previously (Gan & Burfield, 1989). Table 3.7 shows all the reaction times of Bz-ENR50 with the T_gs and δCp.

As can been seen in Figure 3.9, when ENR50 was heated with acetic acid over a period of about 3 hours, a rapid increased in T_g occurred (5.42°C). A further slow elevation of the T_g was then continued over the next 9 hours. Meanwhile, when the

ENR50 was heated with benzoic acid at elevated temperatures over about 3 hours, a rapid increase in T_g is also occurred (-10.54°C). A further slow elevation of the T_g was continued over the next 7 hours. It is suggested that the increment in T_g with increase in mol% of hydroxyl and ester from Ac-ENR and Bz-ENR could be due to the chain stiffness and intermolecular interaction particularly by the hydrogen bonding as shown in Figure 3.4. Consequently, Ac-ENR50 and Bz-ENR50 with 24 h reaction time become more brittle compared to the sample with less reaction time since the chain segment mobility was more restricted, thus resulted the enhancements of the T_g value.

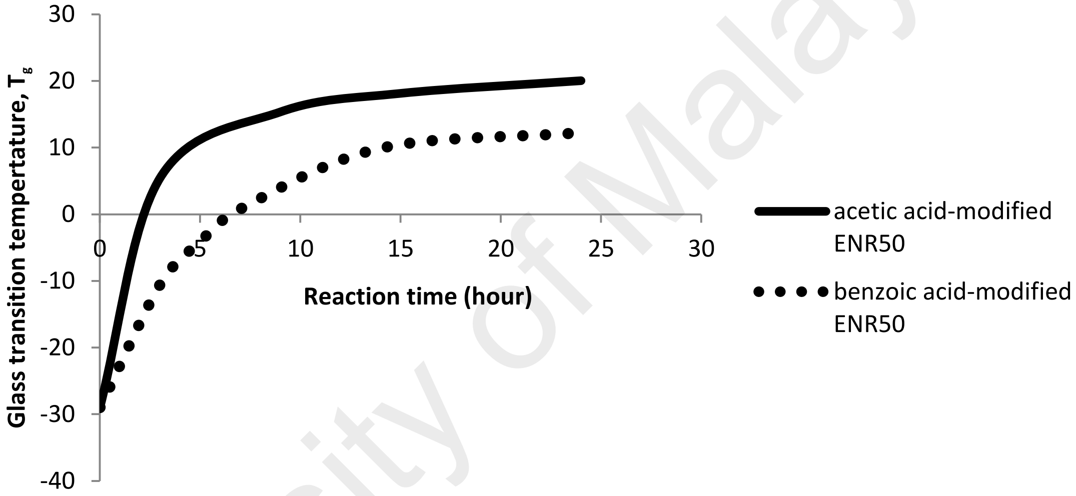


Figure 3.9: Change in T_g with reaction time (hour) for Ac-ENR50 and Bz-ENR50

Table 3.7: Glass transition temperature and δCp of acid-modified ENR50 with different reaction times.

Reaction time (hour)	**Ac-ENR50**		**Bz-ENR50**	
	T_g (°C)	δCp (J/g°C)	T_g (°C)	δCp (J/g°C)
Control	-29.00	0.50	-29.00	0.50
3	5.42	0.51	-10.54	0.81
9	15.34	0.59	2.50	0.42
15	18.13	0.61	9.90	0.60
24	20.03	0.42	12.25	0.60

3.2. Compatibility carboxylic acids-modified ENR50/PEO/$LiClO_4$ blends

3.2.1. Conductivity

The plot of conductivity values of different ratio of carboxylic acid-modified ENR50/PEO with lithium salt at room temperature is shown in Figure 3.10 and the data is tabulated in Table 3.8. Ac-ENR50/PEO/$LiClO_4$ blends samples exhibit the conductivity in the range of 10^{-9} to 10^{-7}. This system shows better conductivity property compare to Bz-ENR50/PEO/$LiClO_4$ blends in the range of 10^{-10} to 10^{-7}.

Ac-ENR50/PEO/$LiClO_4$ blends ratio 30/70/2 exhibits the highest conductivity value of 6.86×10^{-7} S cm^{-1} followed by 4.94×10^{-8} S cm^{-1} for 40/60/2 sample, 2.14×10^{-8} for blends 70/30/2, 3.06×10^{-8} for blends 80/20/2 and 3.59×10^{-9} S cm^{-1} for 90/10/2 sample. Molecular structure of Ac-ENR50 has higher polarity compared to ENR50 which assume to have more coordination sites for Li cation solvation. Thus, it resulted in improved conductivity for Ac-ENR50/PEO with $LiClO_4$ salt.

For Bz-ENR50/PEO 30/70 with $LiClO_4$, the conductivity was 5.80×10^{-7} S cm^{-1} followed by 40/60 sample with 4.26×10^{-8} S cm^{-1}. The conductivity is observed to increase with increase in PEO ratio.

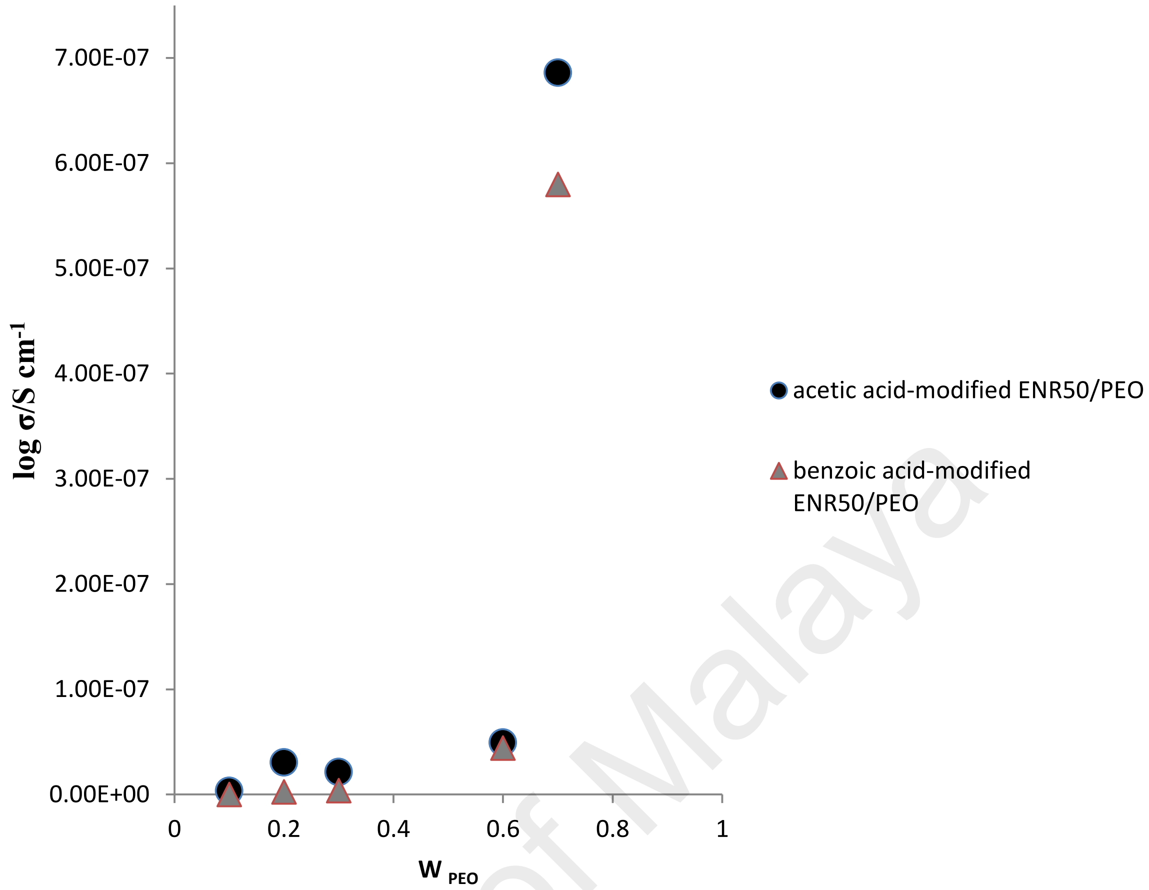


Figure 3.10: Conductivity as a function of weight of PEO for Ac-ENR50/PEO/$LiClO_4$ and Bz-ENR50/PEO/$LiClO_4$

Table 3.8: Conductivity values of carboxylic acid-modified ENR50/PEO with 2% lithium salt at room temperature

samples ratio carboxylic acid-modified ENR50/PEO	**acetic acid-modified ENR50/PEO**	**benzoic acid-modified ENR50/PEO**
0/100	3.25×10^{-5}	3.25×10^{-5}
30/70	6.86×10^{-7}	5.80×10^{-7}
40/60	4.94×10^{-8}	4.42×10^{-8}
70/30	2.14×10^{-8}	3.90×10^{-9}
80/20	3.06×10^{-8}	2.44×10^{-9}
90/10	3.59×10^{-9}	1.87×10^{-10}

Polarity of the materials used for solid polymer electrolyte is one of the key factors for attaining high ionic conductivity and only polymers possessing high dipole moments are suitable candidates (Idris et al., 2001). The conductivity results for carboxylic acid-modified ENR50/PEO with lithium salt blends increased with increasing weight fractions of PEO in the blends as observed in this study. The ether group in the PEO polymer structure plays major role to solvate the Li cation significantly as the weight fraction of PEO in the blend increases. By considering these factors, both Ac-ENR50 and Bz-ENR50 have fulfilled the above criteria to serve the function of polymer electrolyte for potential use in lithium batteries.

3.2.2. Fourier Transform Infrared Spectroscopy

FTIR spectra were recorded in order to investigate the chemical interactions of carboxylic acid-modified ENR50 and PEO blends. The interactions between the ether oxygens of PEO and the hydroxyl protons of carboxylic acid-modified ENR50 can be evaluated by infrared spectroscopy and the information on the specific intermolecular hydrogen bonding interaction between the two components in the blends can be determined.

FTIR was used to compare the Bz-ENR50, Ac-ENR50, PEO and their blends at the following ratio of 30/70, 50/50 and 70/30 for Bz-ENR50/PEO and the ratio of 25/75, 50/50 and 75/25 for Ac-ENR50/PEO.

Figure 3.11 shows spectra of carboxylic acid-modified ENR50/PEO with different ratio of each component. The absorption of hydroxyl groups at 3441 cm^{-1} (Gan & Hamid, 1997) becomes more intense with increase in amount of carboxylic acid-modified ENR50 content in the blends. As no change at this –OH region in all of the blends is observed, it is suggested that there is no interaction happened with each other.

Peak at 2879 cm^{-1} corresponds to the C–H stretching. The intensity of the band increases with increasing PEO content of the blend. This corresponds to the C-H stretching of PEO (Bailey & Koleske, 1976). The absorbance band for carboxylic acid-modified ENR50/PEO 50/50 blends overlaps with the methylene group, -CH$_2$- from Bz-ENR50. The characteristic triplet bands of C–O–C stretching for PEO are observed at 1060, 1094 and 1144 cm^{-1} and they are present in all the blends containing PEO as shown in Figure 3.11. The triplet maintains its intensity and shape while the position of the maximum peak is slightly shifted from 1094 cm^{-1} to 1099 cm^{-1} for Ac-ENR50/PEO 75/25 blend and Bz-ENR50 /PEO 70/30. In view of the resolution of the instrument being 4 cm^{-1}, the peak shift is not indicative of any significant interaction between the two constituents of the blend. There is no reduction in intensity of the two shoulders at 1060 and 1144 cm^{-1} implying that the ability of PEO to crystallize remains unchange with increasing amount of carboxylic acid-modified ENR50.

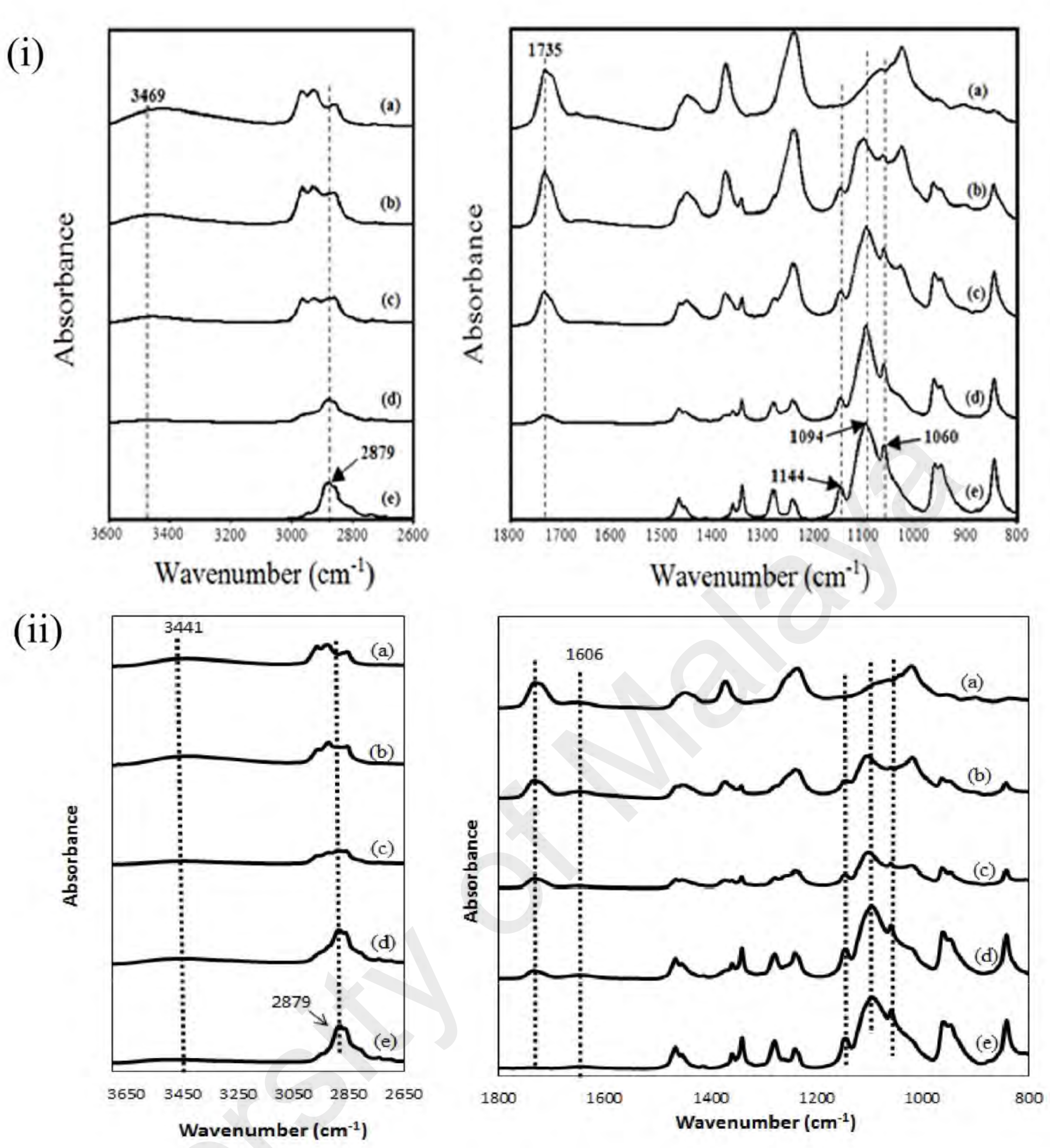


Figure 3.11: FTIR absorbance spectra for (i) Ac-ENR50/PEO blend samples of (a) 100/0, (b) 75/25, (c) 50/50, (d) 25/75 and (e) 0/100. (ii) Bz-ENR50 ENR50/PEO (a) 100/0 (b) 70/30 (c) 50/50 (d) 30/70 and (e) 0/100

The characteristic band of carboxylic acid-modified ENR50 shows a strong absorption band at wavenumber of 1735 cm^{-1} due to the C=O stretching of ester group as shown in Figure 3.11. The intensity of the C=O stretching is proportionate to the amount of the carboxylic acid-modified ENR50 in the blend. Peak at 1606 cm^{-1} indicates aromatic ring pattern increases as the ratio of Bz-ENR50 content increases.

3.2.3. Morphological Studies by Polarizing Optical Microscopy

The miscibility and immiscibility of a semi crystalline/amorphous blend between the components can be evaluated through morphology analysis (Pereira et al., 2011). No crystallization was observed for carboxylic acid-modified ENR50/PEO from 70/30 to 90/10. Blends of carboxylic acid-modified ENR50/PEO from 10/90 to 60/40 exhibited volume filling spherulites at T_c = 39°C after melt reaction at 80°C. Bz-ENR50/PEO/$LiClO_4$ blends exhibited higher G values for PEO spherulites (Figure 3.13) whereas Ac-ENR50/PEO/$LiClO_4$ blends exhibited a lower spherulites growth rate (Figure 3.14) compared to ENR50/PEO (Figure 3.12).

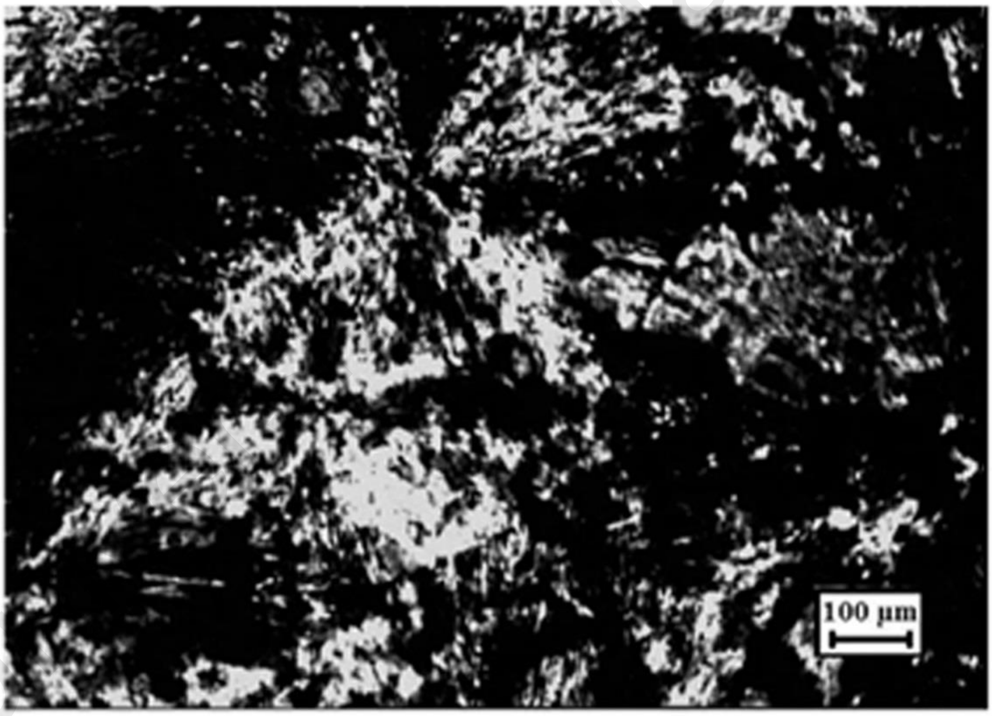


Figure 3.12: Polarizing Optical Microscopy for the blend, ENR50/PEO/$LiClO_4$ 50/50/2

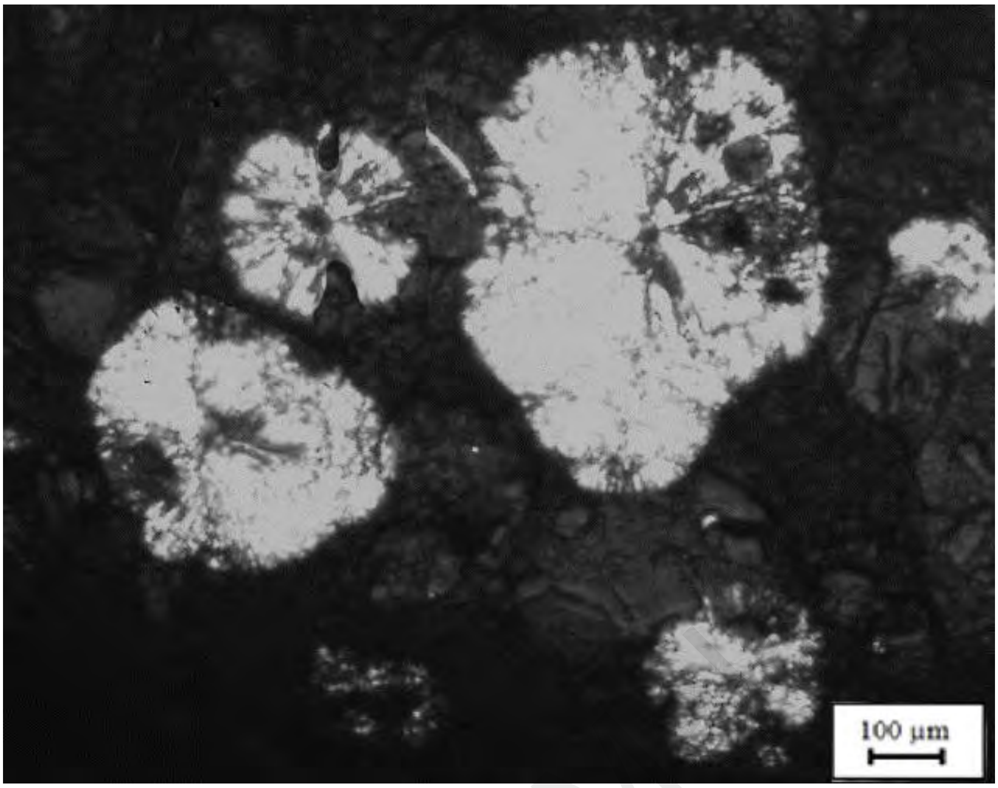


Figure 3.13: Polarizing Optical Microscopy for the blend, Bz-ENR50/PEO/LiClO4 50/50/2

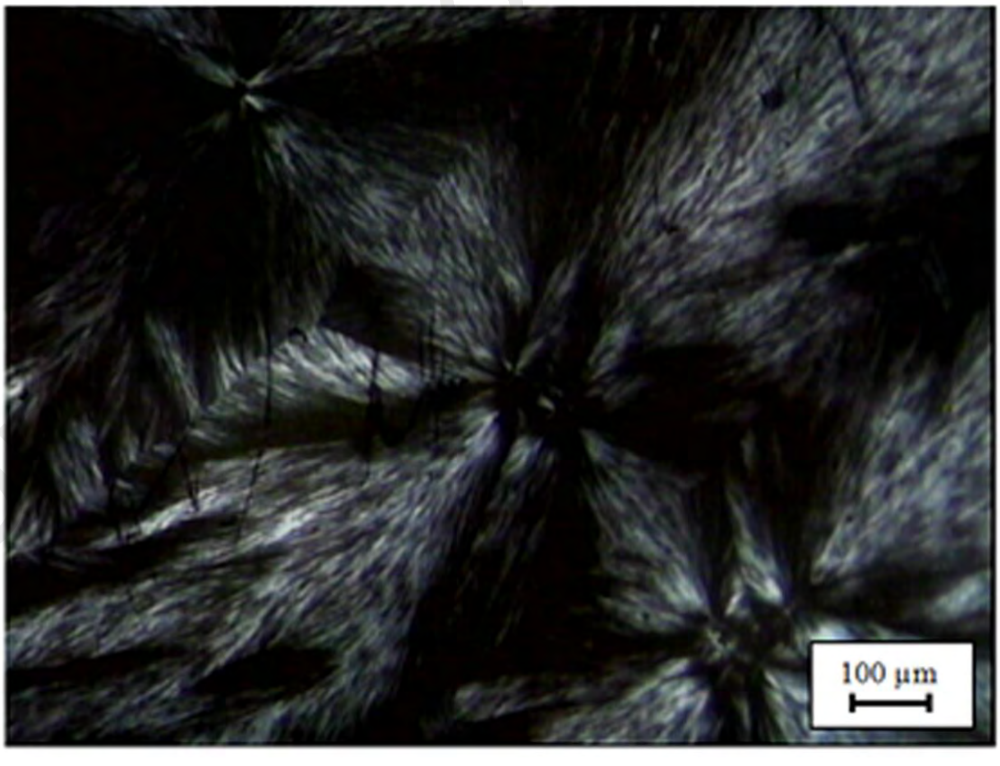


Figure 3.14: Polarizing Optical Microscopy for the blend, Ac-ENR50/PEO/LiClO4 50/50/2

Lower crystallization rate was observed for the Ac-ENR50/PEO/$LiClO_4$ blend. The G values of PEO spherulites in ENR50/PEO/$LiClO_4$ 50/50/2, Bz-ENR50/PEO/$LiClO_4$ 50/50/2 and Ac-ENR50/PEO/$LiClO_4$ 50/50/2 blends were determined by POM and tabulated in Table 3.9.

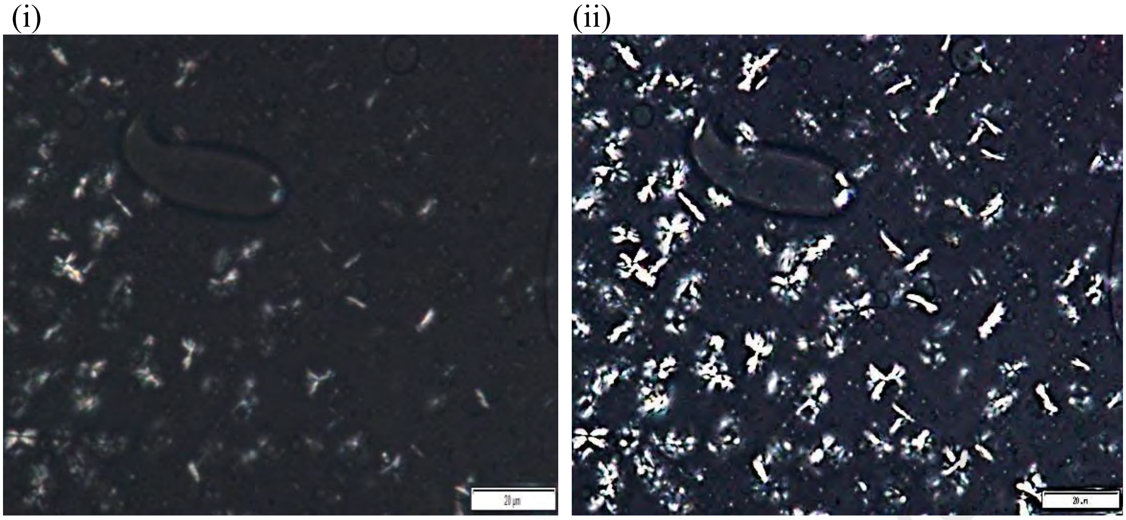
Table 3.9: Radial growth rate of PEO spherulites with different type of blends

Blends	Radial growth rate, G μms^{-1}
ENR50/PEO/$LiClO_4$ (50/50/2)	2.6
Bz-ENR50/PEO/$LiClO_4$ (50/50/2)	3.5
Ac-ENR50/PEO/$LiClO_4$ (50/50/2)	1.3

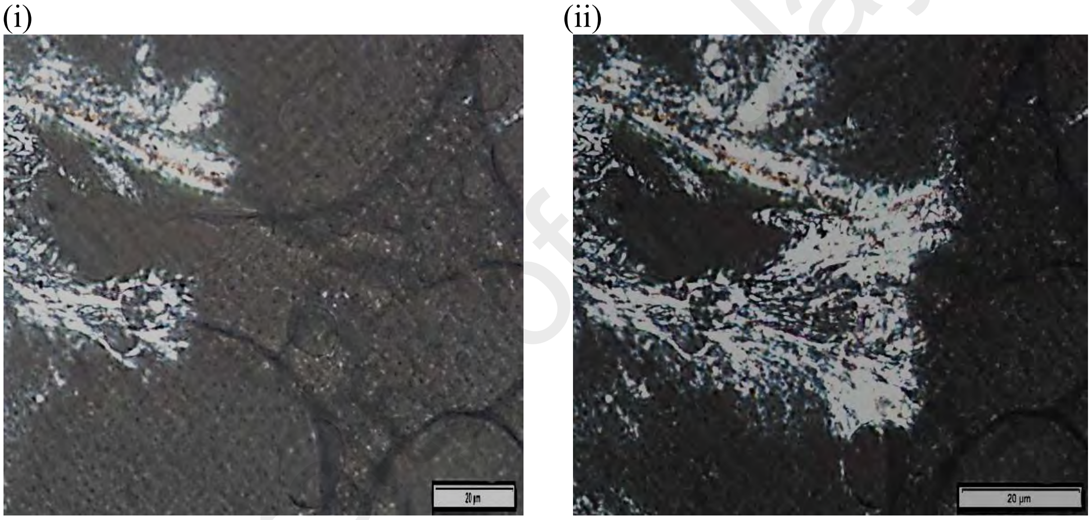
Table 3.9 shows the estimation of radius of growing spherulites, *R* in Bz-ENR50/PEO/$LiClO_4$ (50/50/2) at T_c = 39°C, from the PEO growing spherulites diameter measurements with 15 s time interval. It is found that radius of PEO growing spherulites, *R*, increases linearly as the function of time for Bz-ENR50/PEO/$LiClO_4$ (50/50/2) blend as shown in Figure 3.16.

Figure 3.17 shows POM images of four different ratios of Bz-ENR50/PEO/$LiClO_4$ blends. Volume filling of fibrillary fine texture of the spherulite of PEO is exhibited for Bz-ENR50/PEO/$LiClO_4$ (10/90/2) after melt reaction at T_c = 39°C for 1 h, followed by Bz-ENR50/PEO/$LiClO_4$ (30/70/2). In Bz-ENR50/PEO/$LiClO_4$, 50/50/2 and 60/40/2 blending ratio have led to unclear spherulites. The fibrous textures disappeared gradually with decrease in the content of PEO in blends.

(a) Bz-ENR50/PEO/$LiClO_4$ (10/90/2)



(b) Bz-ENR50/PEO/$LiClO_4$ (50/50/2)



(c) Bz-ENR50/PEO/$LiClO_4$ (60/40/2)

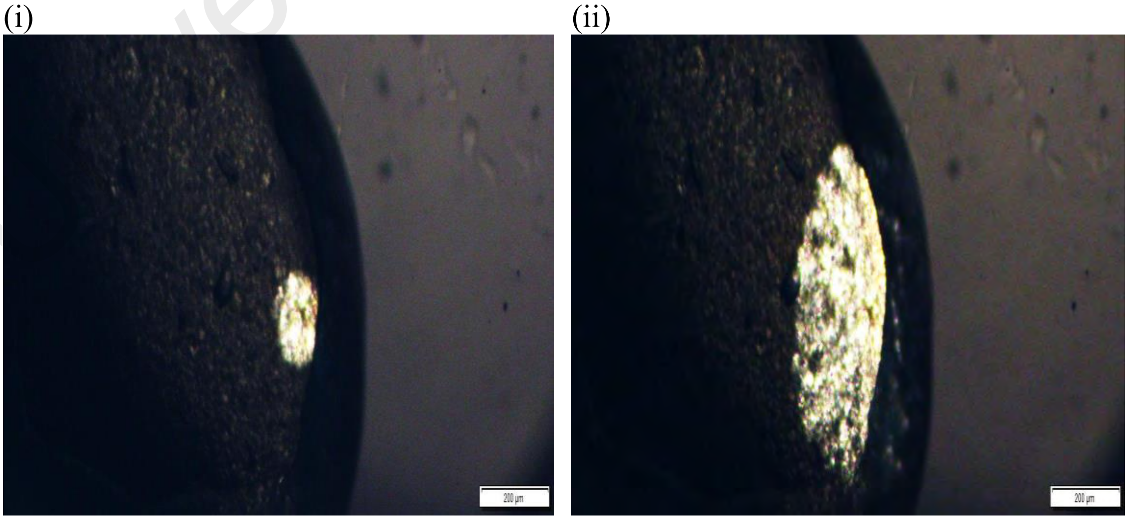


Figure 3.15: Polarizing Optical Microscopy images for Bz-ENR50/PEO/$LiClO_4$ at T_c = 39°C with different ratios and time intervals (i) first time interval (ii) 15 s time interval

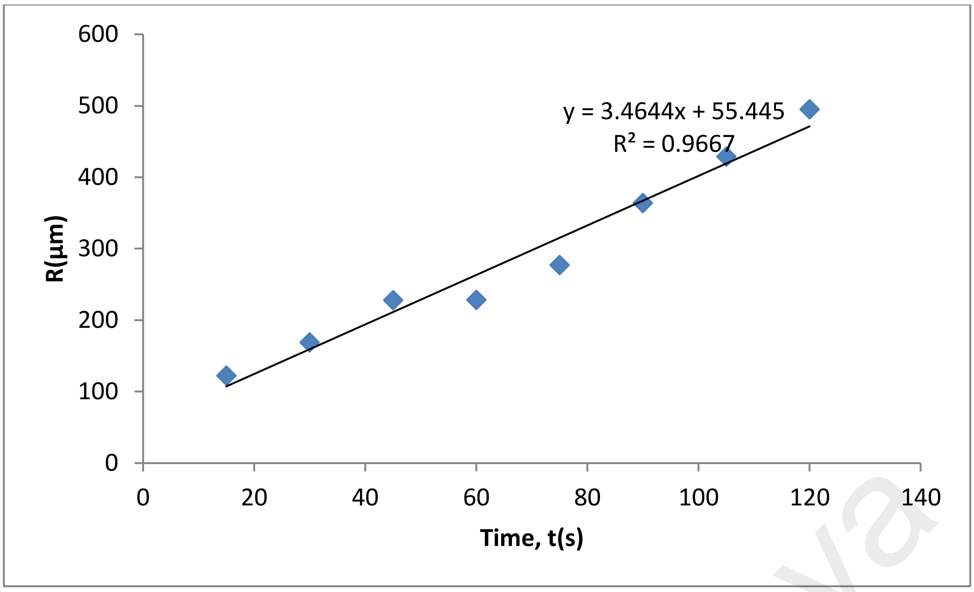
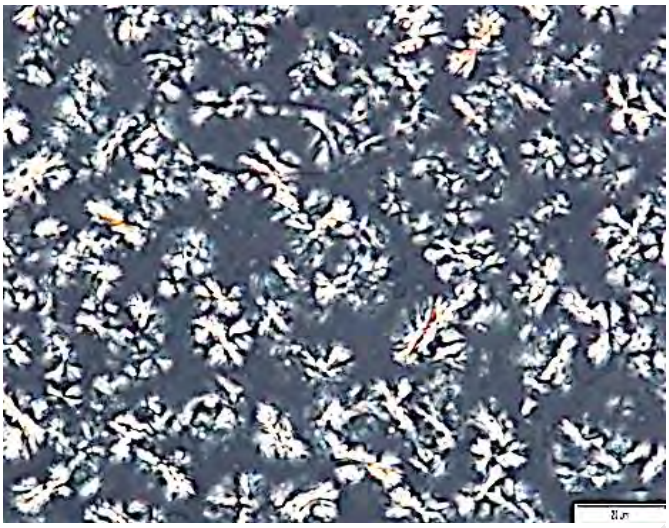


Figure 3.16: Radius of PEO growing spherulites as the function of time for Bz-ENR50/PEO/LiClO$_4$ (50/50/2) blend at T_c =39°C

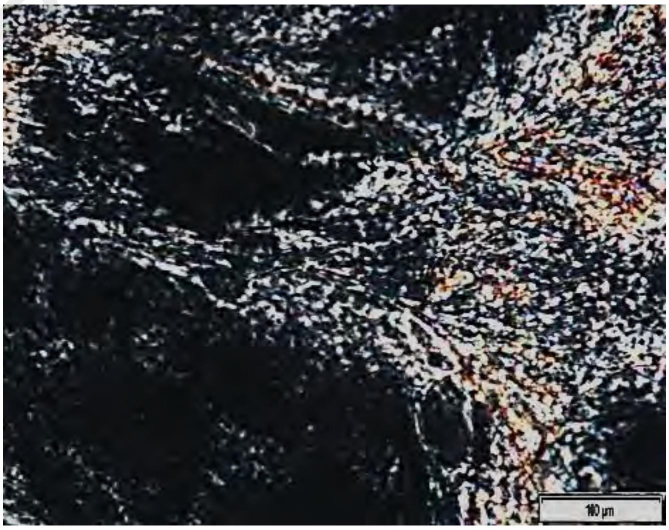
Table 3.10: Diameter and radius for the growing spherulites for Bz-ENR50/PEO/LiClO$_4$ (50/50/2) blend at T_c=39°C with time interval 15 s

		Time interval, t(s)							
		15	30	45	60	75	90	105	120
d(µm)	1	126.3	183.9	233.6	227.0	258.4	342.8	456.8	526.9
	2	119.2	161.1	194.5	207.9	296.1	425.5	410.2	474.1
	3	122.0	162.4	256.3	251.6	277.6	324.0	420.4	484.3
d̄(µm)		122.5	169.1	228.1	228.8	277.4	364.1	429.2	495.1
s(µm)		3.6	12.8	31.2	21.9	18.8	54.0	24.5	28.0
R(µm)		107.4	159.4	211.3	263.3	315.3	367.2	419.2	471.2

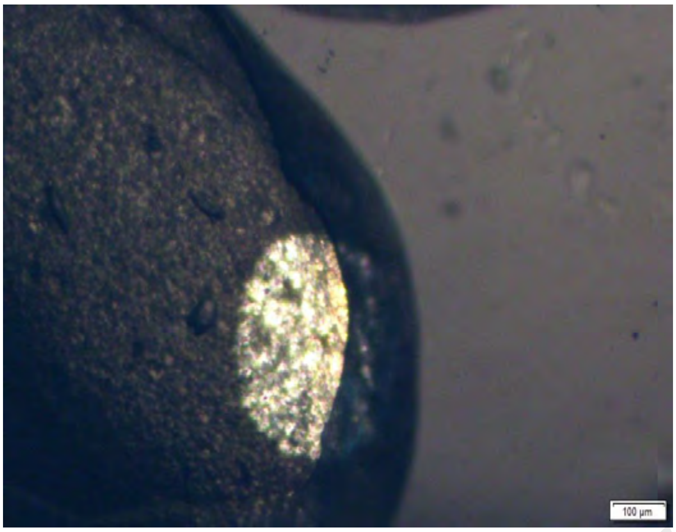
(See Appendix for the calculations)


(a) Bz-ENR50/PEO/LiClO$_4$ (10/90/2)


(b) Bz-ENR50/PEO/LiClO$_4$ (30/70/2)



(c) Bz-ENR50/PEO/LiClO$_4$ (50/50/2)



(d) Bz-ENR50/PEO/$LiClO_4$ (60/40/2)

Figure 3.17: Polarized optical microscopy of Bz-ENR50/PEO/$LiClO_4$ with different blend at 39°C after 1 h.

CHAPTER 4 CONCLUSIONS & SUGGESTIONS FOR FUTURE STUDIES

Chemical modification of ENR50 with carboxylic acid was synthesized by reacting the rubber dissolved in toluene with excess carboxylic acid at high temperature. The reaction proceeded with reduction of epoxide content clearly observable through ^{1}H NMR. Ester and hydroxyl groups present after the modification is a good agreement with FTIR analysis. TGA analysis shows that ENR50 decompose in one single step, while Ac-ENR50 has four degradation steps, and Bz-ENR50 shows 3 steps of degradation. T_g for ENR50 is -29.0^{o}C and T_g for Ac- ENR50 is at 20.0^{o}C while T_g for Bz-ENR50 is at 12.3^{o}C.

Polymeric electrolytes of carboxylic acid-modified ENR50/PEO/$LiClO_4$ have been prepared by solution casting method. The blends were investigated by Impedance spectroscopy and POM was used to estimate the spherulite growth rates. The morphologies studies of blends by POM further confirm the immiscibility of the two components. Bz-ENR50/PEO blends show higher G values for PEO spherulites whereas the Ac-ENR50/PEO blends exhibit a lower spherulites growth rate compared to unmodified ENR50/PEO. The ionic conductivity of the blend increases with the weight fraction of PEO. These novel blends could be conducting polymer electrolytes with potential application in battery.

Another area of interest would be to study the mechanical properties of carboxylic acids-modified ENR50/PEO/$LiClO_4$ blends such as tensile strength, modulus and elongation at break. The high-resolution SEM to compare the surface of these blends before and after tensile drawing also could be determined.

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APPENDIX D : Publications and Paper Presented

Publications:

Wan Nurhidayah A. Karim, Jin Guan Ng, Chin Han Chan & Seng Neon Gan. (2013). Preparation and characterisation of blends of poly(ethylene oxide) and functionalised epoxidised natural rubber. *International Journal of Materials Engineering Innovation*, Vol.4, No.3/4, pp.314 - 324 (SCOPUS-Cited Publication)

Wan Nurhidayah A. Karim, Jin Guan Ng, Chin Han Chan, Rosiyah Yahya & Seng Neon Gan. (2016). Blends of Mono-carboxylic Acid Modified Epoxidized Natural Rubber and Poly(ethylene oxide). *Rubber Chemistry and Technology*. (*In Press*)

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Wan Nurhidayah A Karim, Jin Guan Ng, Chin Han Chan, Yahya. R and Seng Neon Gan, 2011. Proceeding of the 2nd Malaysia Polymer International Conference (oral presenter)

Wan Nurhidayah A Karim, Jin Guan Ng, Chin Han Chan, Yahya. R and Seng Neon Gan, 2011. 7th Mathematics and Physical Sciences Graduate Congress, National University of Singapore.(poster)