STUDIES OF MODIFIED NATURAL RUBBER/EPOXY RESIN BLEND

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การศึกษาพอลิเมอร์ผสมระหว่างยางธรรมชาติดัดแปรและอีพอกซีเรซิน

นางสาวณัฐกฤตา ประเสริฐโสภา

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิศวกรรมศาสตรมหาบัณฑิต
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STUDIES OF MODIFIED NATURAL RUBBER/EPOXY RESIN BLEND

Suranaree University of Technology has approved this thesis submitted in partial fulfillment of the requirements for a Master’s Degree.

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ณัฐกฤตา ประเสริฐโสภา : การศึกษาพอลิเมอร์ผสมระหว่างยางธรรมชาติดัดแปรและอีพอกซีเรซิน (STUDIES OF MODIFIED NATURAL RUBBER/EPOXY RESIN BLEND) อาจารย์ที่ปรึกษา : ผู้ช่วยศาสตราจารย์ ดร.ปราณี ชุมสำโรง, 100 หน้า.

วิทยานิพนธ์นี้ศึกษาการเพิ่มความเหนียวให้กับอีพอกซีเรซินโดยใช้ยางธรรมชาติที่ลดน้ำหนักโมเลกุลและยางธรรมชาติที่ลดน้ำหนักโมเลกุลซึ่งผ่านการกราฟท์เป็นสารเพิ่มความเหนียว การลดน้ำหนักโมเลกุลของยางธรรมชาติเพื่อส่งเสริมการกระจายตัวระดับโมเลกุลในอีพอกซีเรซิน จากการตรวจสอบน้ำหนักโมเลกุลด้วยเครื่องเจลเพอร์มีเอเบิลโครมาโตกราฟฟี (GPC) พบว่าน้ำหนักโมเลกุลและการกระจายน้ำหนักโมเลกุลของยางธรรมชาติที่ลดน้ำหนักโมเลกุล มีค่าเป็น 55,984 กรัม/โมล และ 2.420 ตามลำดับ

ในกระบวนการกราฟท์ใช้มอนอเมอร์ผสมระหว่างเมทิลเมทาคริเลต (MMA) และไกลซิดิลเมทาคริเลต (GMA) ที่อัตราส่วนผสมเท่ากับ 90 : 10 เปอร์เซ็นต์โดยน้ำหนัก ปัจจัยที่ศึกษาในกระบวนการกราฟท์ คือ ชนิดของตัวริเริ่มปฏิกิริยา ปริมาณของตัวริเริ่มปฏิกิริยา และปริมาณของมอนอเมอร์ผสมที่มีต่อองศาการกราฟท์ จากการตรวจสอบด้วยเครื่องนิวเคลียร์แมกเนติกเรโซแนนซ์ พบว่าเบนโซอิลเปอร์ออกไซด์ (BPO) ให้องศาการกราฟท์สูงกว่าเอโซบิสไอโซบิวทิโรไนไตรล์ (AIBN) แต่ยางธรรมชาติที่ลดน้ำหนักโมเลกุลและผ่านการกราฟท์ด้วย BPO ไม่ละลายในอีพอกซีเรซิน AIBN ให้องศาการกราฟท์สูงสุดเมื่อใช้ในปริมาณเท่ากับ 2 ส่วนใน 100 ส่วน (phr) ของยางธรรมชาติที่ลดน้ำหนักโมเลกุล และองศาการกราฟท์เพิ่มขึ้นตามปริมาณมอนอเมอร์ที่เพิ่มขึ้น จากการตรวจสอบน้ำหนักโมเลกุลของยางธรรมชาติที่ลดน้ำหนักโมเลกุลซึ่งผ่านการกราฟท์พบว่าน้ำหนักโมเลกุลลดลงตามปริมาณมอนอเมอร์ที่เพิ่มขึ้น

การตรวจสอบสมบัติเชิงกลของพอลิเมอร์ผสมระหว่างอีพอกซีเรซินกับยางธรรมชาติที่ลดน้ำหนักโมเลกุลซึ่งผ่านและไม่ผ่านการกราฟท์ทำโดยการทดสอบค่าความต้านทานต่อแรงกระแทกและความต้านทานต่อการดัดโค้ง จากผลการทดสอบพบว่าพอลิเมอร์ผสมที่มีปริมาณยางเท่ากับ 1 phr แสดงค่าความต้านทานต่อแรงกระแทกสูงที่สุด ค่ามอดุลัสดัดโค้งและค่าความต้านทานแรงดัดโค้งลดลงตามปริมาณยางที่เพิ่มขึ้น และค่าความต้านทานต่อแรงกระแทกของพอลิเมอร์ผสมที่ใช้ยางธรรมชาติที่ลดน้ำหนักโมเลกุลซึ่งผ่านการกราฟท์มีค่าสูงกว่าค่าความต้านทานต่อแรงกระแทกของพอลิเมอร์ผสมที่ใช้ยางที่ไม่ผ่านการกราฟท์ และโดยทั่วไป ค่าความต้านต่อแรงกระแทกมีแนวโน้มเพิ่มขึ้นตามการเพิ่มองศาการกราฟท์

นอกจากนี้ จากผลการทดสอบสมบัติเชิงกลของพอลิเมอร์เชิงประกอบที่เตรียมจากพอลิเมอร์ผสมที่แสดงค่าความต้านทานต่อแรงกระแทกสูงที่สุดกับเส้นใยแก้วที่ปริมาณเส้นใยเท่ากับ 5 เปอร์เซ็นต์โดยน้ำหนัก พฟบว่าพอลิเมอร์เชิงประกอบนั้นมีค่ามอดุลัสดัดโค้งและค่าความต้านทานต่อแรงกระแทกสูงกว่าอีพอกซีเรซิน

สาขาวิชา วิศวกรรมพอลิเมอร์
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ลายมือชื่อนักศึกษา________________________
ลายมือชื่ออาจารย์ที่ปรึกษา__________________
ลายมือชื่ออาจารย์ที่ปรึกษาร่วม_______________

NATKRITA PRASOETSOPHA : STUDIES OF MODIFIED NATURAL RUBBER/EPOXY RESIN BLEND. THESIS ADVISOR : ASST. PROF. PRANEE CHUMSAMRONG, Ph.D., 100 PP.

EPOXY/ GRAFTED DEPOLYMERIZED NATURAL RUBBER/ METHYL METHACRYLATE/ GLYCIDYL METHACRYLATE

In this thesis, depolymerized natural rubber (DNR) and grafted depolymerized natural rubber (GDNR) were used as toughening agent for epoxy resin. Natural rubber was depolymerized because rubber needed to be initially molecularly dispersed in epoxy resin. The molecular weight and molecular weight distribution of DNR, which were characterized using gel permeation chromatography (GPC), were 55,984 g/mol and 2.420, respectively.

DNR was grafted with monomer mixture of methyl methacrylate (MMA)/ glycidyl methacrylate (GMA) (90/10 wt/wt%). The effects of types of initiator, initiator concentration and monomer concentration on the degree of graftization of DNR were investigated. The results obtained from nuclear magnetic resonance spectroscopy showed that benzoyl peroxide (BPO) led to a higher degree of graftization than azo-bis-isobutyronitrile (AIBN). However, GDNR prepared using BPO did not completely dissolve in epoxy resin. The degree of graftization reached the maximum at 2 phr of AIBN and increased with increasing monomer concentration. The results from GPC showed that molecular weight of GDNR decreased with an increase of monomer concentration.

Mechanical properties of DNR/epoxy and GDNR/epoxy resin blends were investigated using impact and flexural tests. The results proved that the blend containing 1 phr of DNR showed the highest impact strength. Flexural modulus and flexural strength decreased with increasing rubber content. In addition, impact strength of GDNR/epoxy resin blends was higher than that of DNR/epoxy resin blends. Generally, impact strength tended to increase with increasing degree of graftization.

Moreover, the result from mechanical testing revealed that the composite of the blend with 5 wt% fiber glass possessed higher impact strength and flexural modulus than neat epoxy resin.

School of Polymer Engineering　　Student's Signature____________________

Academic Year 2009　　Advisor's Signature____________________

Co-advisor's Signature__________________

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Natkrita Prasoetsopha

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SYMBOLS AND ABBREVIATIONS

% = Percent

°C = Degree Celsius

µm = Micrometer

AIBN = Azo-bis-isobutyronitrile

BPO = Benzoyl peroxide

DNR = Depolymerized natural rubber

g = Gram

GDNR = Grafted depolymerized natural rubber

GF = Fiber glass

GMA = Glycidyl methacrylate

GPa = Gigapascal

GPC = Gel permeation chromatography

h = Hour

^{1}H-NMR = Proton nuclear magnetic resonance

J = Joule

kJ = Kilo Joule

kN = Kilo newton

kV = Kilo volt

m^2 = Square meter

MHz = Mega hertz

min = Minute

SYMBOLS AND ABBREVIATIONS (Continued)

ml = Milliliter

mm = Millimeter

M_n = Number average molecular weight

mol = Mole

MPa = Megapascal

M_w = Weight average molecular weight

MWD = Molecular weight distribution

phr = Parts per hundred resin

ppm = Parts per million in frequency (for ^{1}H-NMR) and Parts per million (for concentration)

rpm = Revolution per minute

sec = Second

SEM = Scanning electron microscope

wt% = Weight percentage

wt/v = Weight by volume

wt/wt = Weight by weight

30_2AIBN(L) = Example of nomenclature used to identify individual GDNR types. ‘30’ denotes amount of monomer used in phr of rubber. The following digit denotes amount of initiator based on rubber content. ‘AIBN’ denotes type of initiator used to prepare GDNR. ‘L’ denotes large scale preparation (but if small scale preparation, this letter is omitted).

SYMBOLS AND ABBREVIATIONS (Continued)

1_DNR = Example of nomenclature used to identify individual DNR/epoxy resin blend. ‘1’ denotes amount of DNR used in phr.

1_20_2AIBN(L) = Example of nomenclature used to identify individual DNR/epoxy resin blend. ‘1’ denotes amount of GDNR used in phr. ‘20_2AIBN(L)’ denote GDNR types in the blend.

1_DNR_5% GF = Example of nomenclature used to identify individual (G)DNR/epoxy composites. ‘1’ denotes amount of rubber used in phr. ‘DNR’ denote types of rubber in the composites. ‘5% GF’ denote amount of 5 wt% fiber glass used.

CHAPTER I

INTRODUCTION

1.1 General introduction

Epoxy resins are very important class of thermosetting polymers that exhibit high tensile strength and modulus, excellent chemical and corrosion resistance, good dimensional stability, low creep and reasonable performance at elevated temperature. Hence, they are widely used in structural adhesives, surface coatings, electrical laminates and as matrix resins for fiber reinforced composite materials. However, such characteristics in an epoxy require moderate to high levels of crosslinking which can and usually does result in brittle behavior.

As pure materials, epoxy resins have low fracture energy, which is typically less than 200 J/m^2 (Arends, 1996). Therefore, toughening of epoxy resin has been the subject of intense investigation.

Toughness improvement for epoxy resins can be achieved using various rubbers (Saadati, Baharvand, Rahimi, and Morshedian, 2005; Ramos, Costa, Soares, and Nascimento, 2005), engineering thermoplastics (Jin and Park, 2007), interpenetrating polymer networks (IPNs) (Zhi-hua, Yao-peng, Dong-yan, and Zi-qiao, 2008) or inorganic particles (Zhou, Wu, Cheng, Ingram, and Jeelani, 2008). Among these, blending epoxy resin with reactive liquid rubber such as carboxyl-terminated butadiene acrylonitrile copolymer, CTBN (Ramos et al., 2005), amine-terminated butadiene acrylonitrile copolymer, ATBN (Chikhi, Fellahi, and Bakar,

2002) and hydroxyl-terminated polybutadiene, HTPB (Saadati et al., 2005) showed substantial toughness enhancement.

Apart from reactive liquid rubber, liquid rubber containing chemical groups can be used to obtain a significant increase in toughness as well. This was proposed by Huang and Kinloch (1992) and Ismail et al. (2006). For liquid rubber/epoxy blends, liquid rubber is initially dispersed on a molecular level in an epoxy and encouraged to precipitate out when epoxy crosslinking occurs. Then, in cured state, rubber is present as particles in epoxy matrix. The reactive sites or chemical groups promote better adhesion across rubber particle-the matrix interface leading to efficient stress transfer by which a significant increase in toughness is obtained.

Liquid rubber used in toughness enhancement of epoxy resin is normally derived from synthetic rubber. However, there is currently increasing awareness of environmental issues, and this has created a high level of interest in natural rubber (NR) and its derivatives. This is implied by volume of natural rubber produced in year 2002 to year 2006 as shown in Table 1.1.

Natural rubber has attracted great interest because it is a renewable resource, whereas its synthetic counter parts are mostly manufactured from non-renewable oil-based resources.

Also, natural rubber can be used as impact modifier for polymers (Charmondusit, Kiatkamjornwong, and Prasassarakich, 1998). Several studies have been done on toughening epoxy resin using natural rubber (Chuayjuljit, Soatthiyanon, and Potiyaraj, 2006; Ismail et al., 2006; Kumar and Kothandaraman, 2008).

Table 1.1 The total production, export, domestic use and stock of natural rubber of Thailand from 2002-2006 (Rubber Research Institute of Thailand, 2007).

Year	Total Production (Tonnes)	Export (Tonnes)	Domestic Use (Tonnes)	Stock (Tonnes)
2002	2,615,104	2,354,416	278,355	196,680
2003	2,876,005	2,573,450	298,699	202,240
2004	2,984,293	2,637,096	318,649	232,560
2005	2,937,158	2,632,398	334,649	204,256
2006	3,136,993	2,771,673	320,885	249,895

As previously discussed, rubber needs to be initially molecularly dispersed in epoxy resin. This can be done by increasing polarity of natural rubber or reducing molecular weight of rubber. Molecular weight of natural rubber can be reduced either by ozonolysis (Nor and Ebdon, 2000), photolysis (Suksawad and Sakdapipanich, 2005), or chemical depolymerization (Tanaka et al., 1999). In addition, in order to achieve an efficient stress transfer between the rubber and the matrix, rubber must have functional groups which can form chemical bonds with epoxy matrix or can promote interfacial adhesion between rubber particle and matrix. Natural rubber can be functionalized either by epoxidation or grafting with various monomers. Monomers including methyl methacrylate and maleic anhydride are the most frequently studied (Charmondusit et al., 1998; Nakason, Kaesaman, and Supasanthitikul, 2004).

In this work, depolymerized natural rubber was prepared and grafted with methyl methacrylate (MMA) and glycidyl methacrylate (GMA). Depolymerized and grafted depolymerized natural rubbers were used as toughening agents for epoxy resin and fiber glass/epoxy composites.

1.2 Research objectives

The objectives of this study are:

(i) to study the effects of monomer concentration, initiator concentration and types of initiator on the degree of graftization of depolymerized natural rubber grafted with MMA/GMA.

(ii) to study the effects of depolymerized natural rubber (DNR) content on morphological and mechanical properties of DNR/epoxy resin blends.

(iii) to study the effects of degree of graftization of grafted depolymerized natural rubber (GDNR) on morphological and mechanical properties of GDNR/epoxy resin blends.

1.3 Scope and limitation of the study

In this study, the depolymerized natural rubber (DNR) was prepared by a depolymerization process of natural rubber by adding natural rubber latex to methyl ethyl ketone, and then the resulting mixture was subjected to air oxidation in the presence of a potassium persulfate at 70°C. The DNR product was grafted with monomer mixture of methyl methacrylate/glycidyl methacrylate (90/10 wt/wt%) in toluene solution at 80°C. The amounts of monomer mixture in the grafting process were 20, 30, 50 and 75% by weight based on DNR content. The amounts of initiator used were 1, 2 and 3% by weight based on DNR content. Furthermore, the effect of types of initiator was compared between AIBN and BPO at 50 phr of monomer mixture. Molecular weight and molecular weight distribution of DNR and GDNR were determined by gel permeation chromatography. The molecular structure of DNR and GDNR was characterized by nuclear magnetic resonance spectroscopy. DNR was blended with epoxy resin in an amount of 0.5, 1, 2 and 3 parts per hundred of epoxy resin (phr). Blending formulation that showed the highest impact strength was chosen to study the effect of degree of graftization. (G)DNR/epoxy blends which possessed the highest impact strength were applied as matrix for preparation of fiber glass/epoxy composites. The neat epoxy, (G)DNR/epoxy blends and (G)DNR/fiber glass/epoxy composites were prepared by hand lay-up process.

The universal testing machine and basic pendulum impact tester were used to study the mechanical properties of neat epoxy, (G)DNR/epoxy blends and (G)DNR/fiber glass/epoxy composites. Morphology of the fracture surfaces of the neat epoxy, (G)DNR/epoxy blends and fiber glass/(G)DNR/epoxy composites was analyzed using scanning electron microscopy (SEM).

CHAPTER II

LITERATURE REVIEW

Highly crosslinked epoxy resin for engineering applications is normally strong but brittle. Therefore, many attempts have been made to improve toughness of epoxy resin (Ratna, 2001; Kong, Ning, and Tang, 2006; Zhou et al., 2008; Kumar and Kothandaraman, 2008). One of the most successful methods is the use of reactive liquid rubber (Collyer, 1994). In this work, the studies of using liquid natural rubber and modified liquid natural rubber as toughness enhancement materials for epoxy resins were focused.

2.1 Epoxy resins

Epoxy resins are reactive chemicals which are combined with other chemicals known as hardener or curing agent such as triethylenetetramine (TETA) and 4,4´-diaminodiphenylsulfone (DDS) to give systems capable of conversion to predetermined thermoset products. Some commercial epoxy resins and examples of important hardener are discussed below.

2.1.1 Commercial types of epoxy resins

2.1.1.1 Diglycidyl ether of bisphenol A

The most widely used epoxy resins are diglycidyl ethers of bisphenol A, DGEBA (Figure 2.1). These are produced by the reaction of bisphenol A and epichlorohydrin in the presence of sodium hydroxide.

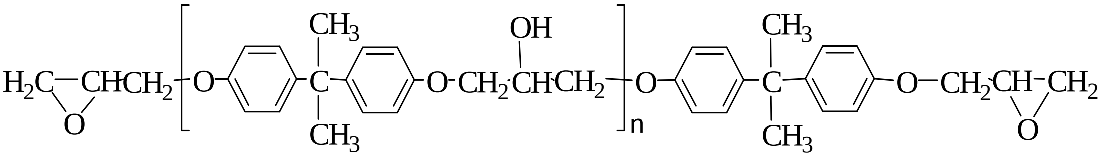


Figure 2.1 Chemical structure of bisphenol A based epoxy resins (Irfan, 1998).

2.1.1.2 Bisphenol F based epoxy resins

Instead of reacting bisphenol A with epichlorohydrin to form a liquid resin, a similar reaction can be conducted between bisphenol F and epichlorohydrin. Figure 2.2 shows the chemical structure of bisphenol F based epoxy resins.

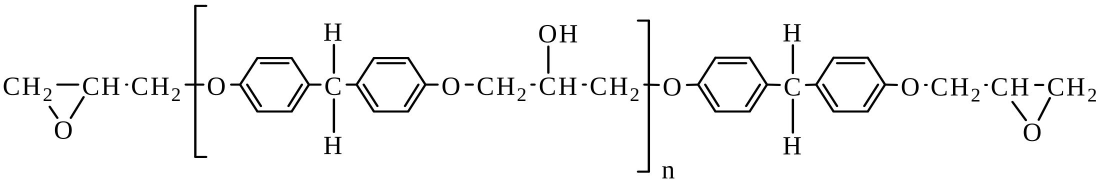


Figure 2.2 Chemical structure of bisphenol F based epoxy resins (Irfan, 1998).

2.1.1.3 Hydantoin resins

In recent years, the hydantoin resins (Figure 2.3) have shown greater popularity for increasing temperature resistance and improving mechanical properties, particularly in structural composites. However, this type of epoxy has presented toxicity problems. At least one hydantoin based product is being supplied for commercial applications, but it requires special handling precautions.

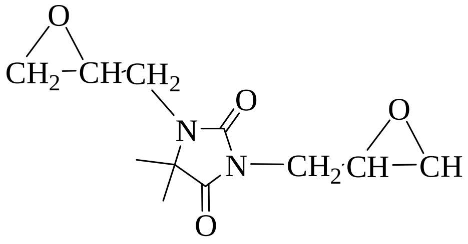


Figure 2.3 Chemical structure of hydantoin resins (Goodman, 1998).

2.1.1.4 Novolacs

Novolacs are epoxidized phenol-formaldehyde or substituted phenol-formaldehyde resins. Chemical structure of novolacs is shown in Figure 2.4.

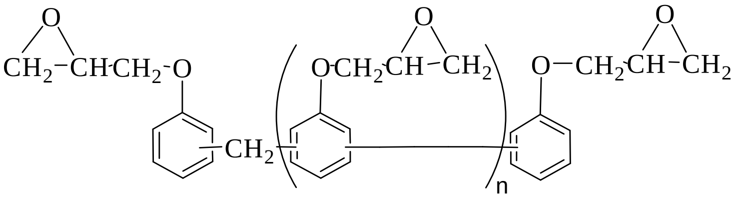


Figure 2.4 Chemical structure of novolacs (Goodman, 1998).

2.1.1.5 Peracid resins

Of the peracid resins the cyclic types contribute to higher crosslink densities. These resins have lower viscosities and color compared to novolac and DGEBA types. Such a typical resin is illustrated by the structure of 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexane carboxylate as shown in Figure 2.5.

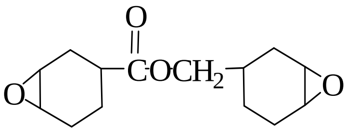


Figure 2.5 Chemical structure of peracid resins (Goodman, 1998).

2.1.2 Characterization of uncured epoxy resins

Epoxy resin used in the present work is modified diglycidyl ether of bisphenol A. Hence, the characterizations of uncured glycidyl ether type epoxy resins are described as follows:

2.1.2.1 Viscosity

The viscosity of epoxy resin is an important property to be considered in handling of the resins. It depends on the temperature, molecular weight, molecular weight distribution and chemical component of the resin. An increase in temperature reduces the viscosity. The presence of high molecular weight species increases the viscosity.

2.1.2.2 Epoxide equivalent weight

Epoxide equivalent weight, EEW, is the value that determines the amount of epoxy groups. It is the weight of resin (in grams) containing 1 gram chemical equivalent epoxy. For a pure diglycidyl ether with two epoxy groups per molecule, the epoxide equivalent will be half the molecular weight, EEW = 170. An example of EEW calculation for pure diglycidyl ether with two epoxy groups per molecule is described as follows:

Molecular weight of diglycidyl ether:

21 carbons = 21 x 12 = 252
24 hydrogens = 24 x 1 = 24
4 oxygens = 4 x 16 = 64

Molecular weight (g/mol) = 340

There are two epoxides functionally active.

Therefore,

$$\mathrm{EEW} = \frac{\text{Molecular weight of DGEBA}}{\text{No. of active epoxide group}}$$

$$= \frac{340\ \text{g/mol}}{2\ \text{equivalent/mol}}$$

$$= 170\ \text{g/equivalent}$$

Epoxide equivalent can be determined by reacting a known quantity of resin with hydrochloric acid and measuring the unconsumed acid by back titration. Table 2.1 shows the relationship between average molecular weight, EEW, and melting point of some commercial glycidyl ether resins.

2.1.2.3 Hydroxyl equivalent

The hydroxyl equivalent is the weight of resin containing one equivalent weight of hydroxyl groups that could be determined by reacting the resin with acetyl chloride in a similar manner as the epoxide equivalent.

Table 2.1 Typical data for some commercial glycidyl ether resins (Chiraphaphisarn, 1997).

Resin	**Average molecular weight (g/mol)**	**Epoxide equivalent weight**	**Melting point (^{o}C)**
A	350-400	175-210	-
B	450	225-290	-
C	700	300-375	40-50
D	950	450-525	64-76
E	1400	870-1025	95-105
F	2900	1650-2050	125-132
G	3800	2400-4000	145-155

2.1.2.4 Iodine number

The iodine number is the number of milligrammes of iodine absorbed by one gramme of the compound. It is a measure of the unsaturation of the epoxy molecule.

2.1.2.5 Colour

The colour of epoxy resins is normally expressed in Gardner colour units, Gardner 1-5 are pale straw colours, Gardner 5-12 are significantly yellow, Gardner 12+ are darker coloured (but translucent).

2.1.2.6 Structure

The structure of the resin is a determining factor for the physical and chemical properties. The number and location of the reactive sites determine the functionality and the crosslinking density.

2.1.3 Curing agents (Hardeners)

Curing agents or hardeners are chemically active compounds which convert epoxy resins into hard, infusible thermosets. They promote the crosslinking reaction either by polyaddition or by homopolymerisation (Irfan, 1998). Four commonly used curing agents can be divided into the following.

2.1.3.1 Amine curing agents

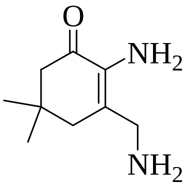
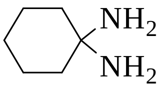
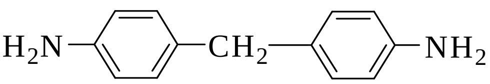
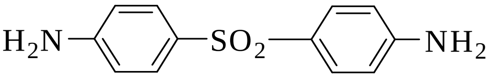
Amine is an important curing agent for epoxy resins and can be divided into three groups.

First, aliphatic amine and derivatives, these are low-viscosity materials with high reactivity and fast cure at ambient temperatures. Aliphatic amines are used principally in civil engineering applications such as in patch repair systems, adhesives, floorings, high solid coatings and grouts. Some examples of aliphatic amine curing agents are primary aliphatic amines e.g. diethylenetriamine (DETA) and triethylenetetramine (TETA).

Second group includes cycloaliphatic and tertiary aliphatic amines. This group of curing agents is used at milder conditions than the aromatics amine but give elevated-temperature performance and chemical resistance of cured resins. They have found usage in adhesive and coating applications.

Lastly, aromatic amines such as 4,4´-diaminodiphenylsulfone (DDS), 4,4´-diamino diphenyl methane (DDM) and m-phenylenediamine (MPDA) are used to cure epoxy resins at high temperatures and at long cure times resulting from the rigid benzene ring in their structure. The aromatic amines are widely used in composite fabrication in both wet and dry lay-up application for filament winding, electrical, piping and tooling. Some examples of commercial curing agents are presented in Table 2.2.

Table 2.2 Commercial curing agents (Mark, 2003).

Formula	Name	Abbreviation
Aliphatic amines		
$NH_2CH_2CH_2NHCH_2CH_2NH_2$	Diethylenetriamine	DETA
$NH_2CH_2CH_2NHCH_2CH_2NHCH_2CH_2NH_2$	Triethylenetetramine	TETA
Cycloaliphatic amines		
	Isophoronediamine	IPDA
	1,2-Diaminocyclohexane	DACH
Aromatic amines		
	4,4´-Diamino-diphenylmethane	DDM
	4,4´-Diamino-diphenylsulfone	4,4´-DDS

2.1.3.2 Acid anhydride agents

Acid anhydrides are another recognized curing agent for epoxy resin because of their good characteristics such as long pot life, high heat distortion temperature, good physical properties, good electrical properties and giving low exothermic energy for curing. Nevertheless, some of their disadvantages are lower resistance to alkali than amine cured systems. Acid anhydrides are preferred curing agents to acid derivatives as the latter will release more water on cure mechanism leading to formation of foaming in the product.

2.1.3.3 Lewis acid agents

Lewis acid such as boron trifluoride in the form of monoethylamine complex (BF_3-MEA) can be used as a curing agent for epoxy resins. BF_3-MEA is characterized by a long pot life and a high glass transition temperature (T_g). Samples of DGEBA catalyzed with BF_3-MEA, although showing considerably increased viscosity, are still usable after storage for 6 months at room temperature.

2.1.3.4 Polyamides

Polyamides are extremely versatile curing agents. They are inexpensive, have little color and can be mixed in any ratio. They provide good mechanical properties, exhibit readily workable pot lives, and cure under mild conditions. Amides groups may be considered as carboxylic acids whose hydroxyl groups have been replaced by a basic group derived from ammonia. The polyamides are generally employed with the glycidyl ether epoxy resins and are less frequently used, if at all, with the epoxidized olefin type (Lee and Neville, 1982).

2.2 Natural rubber

One of the most important polymeric materials is natural rubber (NR) which contains 93-94% *cis*-1,4-polyisoprene (Figure 2.6). NR latex is the form in which rubber is exuded from the *Hevea brasiliensis* tree as an aqueous emulsion. The rubber particles range in size from about 50 Å to about 30,000 Å (3μm). Exceptionally particles up to 5 or 6 μm in diameter are found. The molecular weight (MW) is normally in the range of 10^4-10^7g/mol, depending on the age of the rubber tree, weather, method of rubber isolation and other factors. The polydispersity of MW is usually in the region of 2.5-10 (Bhowmick and Stephens, 2001).

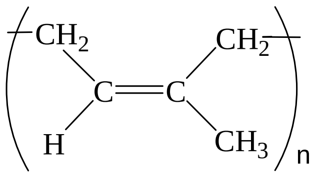


Figure 2.6 Chemical structure of *cis* 1,4-polyisoprene.

The advantages of NR are outstanding flexibility, excellent heat built up properties and high mechanical strength. Moreover, it is a renewable resource, whereas its synthetic counterparts are mostly manufactured from non renewable oil-based resources (Nakason, Kaesaman, and Yimwan, 2003). Therefore, NR has created a high level of interest in using it and its derivatives. Examples of works that have focused on NR uses are discussed below.

Thongpin, Wongtimnoi, Kamolsawat, and Rotkasem (2006) studied binder synthesis from natural rubber for use in making running tracks in Thailand via UV-irradiation.

Suriyachi, Kiatkamjornwong, and Prasassarakich (2004) prepared natural rubber grafted with glcidyl methacarylate and styrene. The grafted NR was used as a compatibilizer in NR and poly(methylmethacrylate) blends for the fabrication of automobile components.

In 2007, Siri-Upathum and Boonyawat proposed the method of reducing allergenic rubber protein in the natural rubber latex for rubber glove production.

Moreover, there are many research works that have concentrated on using NR as impact modifier for polymer. In 1998, Charmondusit et al. grafted copolymer of methyl methacrylate and styrene onto natural rubber using emulsion process. The grafted natural rubber product could be used as an impact modifier for polyvinylchloride, PVC.

Chuayjuljit et al. (2006) used epoxidized natural rubber, ENR, as impact modifier for epoxy resin. The impact strength of epoxy resin could be improved by blending with ENR.

Recently, Kumar and Kothandaraman (2008) modified diglycidyl ether of bisphenol A (DGEBA) type epoxy resin with maleated depolymerized natural rubber, MDPR. The addition of MDPR into epoxy resin resulted in an increase in the elongation at break, flexural strain to failure and impact strength.

As mentioned above, NR used as impact modifier for epoxy resin is epoxidized NR or depolymerized NR. NR was applied in that form because it must have polarity or be a low molecular weight polymer in order to initially molecularly disperse in epoxy matrix.

2.3 Depolymerization of natural rubber

Depolymerization of polymer is based on a reaction in which a reagent with reactive polar groups opens the active linkage in the polymer backbone. It can reduce chain length of polymer. Natural rubber that is subjected to depolymerization is called depolymerized natural rubber (DNR) or “liquid natural rubber”. Having strong adhesive power and excellent crosslinking reactivity, it has been used widely as a raw material for adhesives, pressure-sensitive adhesives, sealing materials, caulking compounds and the like. It is now attracting attention in various industrial fields. As compared with solid rubber, liquid rubber is advantageous for the production of various products because it can be easily processed and requires less energy (Tanaka, et al., 1996).

2.3.1 Depolymerization methods

In general, a DNR can be obtained by mastication, photolysis, chemical decomposition or the like of the natural rubber.

Mastication is a method for accelerating reduction in the molecular weight by breaking the rubber molecular chains of the raw rubber through mechanical action and heating in a roller mill or internal mixer, and then adding a peptizing agent such as a mercaptan (Okwu and Akinlabi, 2007).

Suksawad and Sakdapipanich (2005) used photolysis method for breaking the molecular chains with light energy, i.e. ultraviolet light.

Another approach which has been used to reduce molecular weight of natural rubber is chemical decomposition. This method is degradation of molecular chains with chemical reagents. In 1996, Tanaka et al. proposed the process for depolymerizing natural rubber which comprised adding a carbonyl compound to natural rubber latex or deproteinized natural rubber, and then subjecting the resulting natural rubber or deproteinized natural rubber to air oxidation in the presence of a radical forming agent. The results showed that the depolymerized natural rubber having a narrow molecular weight distribution can be obtained at high reaction efficiency.

2.3.2 Parameters affecting the molecular weight of depolymerized natural rubber

The intensity and the extent of the chain scission reaction depend upon temperature, reaction time and concentration of the degradation agent etc.

Isa et al. (2007) investigated the influence of temperature and reaction time in the thermal degradation of natural rubber latex. They found that the longer reaction times and higher temperature, the lower would be the molecular weight of the products formed.

Nor and Ebdon (2000) studied ozonolysis of natural rubber, described as low protein unvulcanised in diluted chloroform solution at $0^{o}C$. They found that the number average molecular weight of less than 900 g/mol was obtained after 20 min of ozonolysis.

Suksawad and Sakdapipanich (2005) studied photo-chemical degradation of deproteinized natural rubber (DPNR) latex using UV irradiation in the presence of H_2O_2 and TiO_2 film as catalysts. They found that the photodegradation of 10% dry rubber content DPNR latex on TiO_2 coated petri dish in the presence of 20% H_2O_2 with UV light (60 watt) for 5 h gave the low molecular-weight natural rubber with the value of 10^4 g/mol.

Pinyocheep and Duangthong (2000) prepared liquid natural rubber (LNR) using phenylhydrazine/O_2 system. Their results illustrated that the viscosity average molecular weight, M_v, of LNR was varied with the amount of phenylhydrazine. The lowest M_v which they obtained was 4,700 g/mol.

Moreover, Okwu and Akinlabi (2007) used Funtumia latex which is one of the sources of wild rubber in Africa and nitrobenzene as molecular weight depressants for natural rubber. They found that an increasing the amount of Funtumia latex in a blend with natural rubber could produce a lowering of the molecular weight. For the effects of concentration of nitrobenzene and reaction time on the molecular weight of NR, the results showed that an increase in concentration and time gave a decrease of molecular weight.

2.4 Radical graft copolymerization

2.4.1 Graft copolymer synthesis

The synthesis of graft copolymers using free radical polymerization can be divided into groups of related processes: chain transfer and copolymerization, redox polymerization, high-energy radiation techniques and photochemical synthesis (Halasa, Massie, and Ceresa, 2005).

2.4.1.1 Chain transfer and copolymerization

In a free radical polymerization, chain transfer is an important reaction. Chain transfer to a monomer, solvent, mercaptan, or other growing chain can take place. When a chain transfer reaction to another chain takes place, it creates a radical which acts as a site for further chain growth and grafting:

$$P\cdot \quad + \quad P \quad \longrightarrow \quad PH \quad + \quad P\cdot$$

$$R\cdot \quad + \quad P \quad \longrightarrow \quad RH \quad + \quad P\cdot$$

$$P\cdot \quad + \quad P\cdot \quad \longrightarrow \quad PH \quad + \quad P\cdot$$

The reaction proceeds by the transfer of a hydrogen or halogen (in the case of halogenated polymers) atom from a macromolecule P to the growing chains P· (or to an excess initiator free radical R·, thereby "terminating" them). The reactivity is now located on the transfer molecule, which in turn initiates copolymerization, i.e., the growth of a grafted side chain of a newly introduced second monomer. A measure of grafting occurs with most monomer-polymer systems, especially those initiated by benzoyl peroxide, if the concentrations of polymer and initiator are high.

The simplest technique is to dissolve the polymer in the appropriate solvent. Then peroxide initiator, which abstracts hydrogen radical and generates a radical on the polymer chain, is added. After that, fresh monomer is filled for grafting onto this site. This technique has been employed in grafting methylacrylate onto natural rubber and synthetic polyisoprene (Halasa et al., 2005).

2.4.1.2 Redox polymerization

Redox polymerizations are among the most popular techniques for grafting reaction, and of the possible initiator systems, ferrous ion oxidation and those based on ceric ion reduction are widely used. In a redox polymerization, a hydroperoxide or similar group is reduced to a free radical plus an anion, while the metal ion is oxidized to a higher valency state, and at the same time a monomer is added. When the reducible group is attached to a polymeric chain, the free radical grafting sites thus formed on the macro-molecular backbone act as initiators for graft copolymerization (Halasa et al., 2005).

2.4.1.3 High-energy radiation techniques

During high-energy irradiation in vacuo, e.g., from a ^{60}Co source, some main-chain degradation of natural rubber and other polyisoprenes occurs. Much of the irradiation energy is also absorbed by the removal of hydrogen atoms from main chain.

The irradiation of natural rubber in the presence of a vinyl monomer thus leads primarily to a synthesis of graft copolymers, but some block copolymer is certainly always present. Irradiation syntheses may be carried out in solution, either in contact with liquid monomer (with or without a diluent) or in contact with monomer in vapor phase, or in emulsion or suspension. The rubber may be preirradiated in the absence of air to produce free radicals for later monomer addition, but the life of these radicals is short as a result of mobility within the rubber matrix. Irradiation at very low temperatures makes it possible to use the trapped radicals technique for a variety of natural and synthetic rubbers. Polymers with a crystalline phase are more readily preirradiated to initiate later grafting by trapped radicals.

The irradiation of mixed latexes for subsequent combination of the ruptured chains is another approach; it has been carried out with natural rubber and poly(vinyl chloride) latexes to prepare graft and block copolymers in fairly high yields without the problem of monomer recovery (Halasa et al., 2005).

2.4.1.4 Photochemical synthesis

Macromolecules containing photosensitive groups which absorb energy from ultraviolet frequencies often degrade by free radical processes. The degradative process as a rule is fairly slow, but by the addition of photosensitizers, such as xanthone, benzyl, benzoin and 1-chloroanthraquinone, the rate can be speeded up to enable graft copolymerization to take place in the presence of methyl methacrylate or other monomers. This can be done in the case of natural rubber in the latex phase with reasonably high yields of graft copolymer. Natural rubber-g-polystyrene and poly(butadiene-g-styrene) have both been prepared by ultraviolet irradiation of sensitized latex-monomer dispersions. A combination of photochemical synthesis and redox-type initiation can also be carried out, a process known as one-electron oxidation, to achieve grafting with minimal homopolymer formation (Halasa et al., 2005).

2.4.2 Graft copolymerization of natural rubber

As mentioned earlier, natural rubber (NR) possesses excellent physical properties including its high resilience, strength and fatigue resistance. Moreover, it is a renewable resource. However, NR is less resistance to ozone, oxidation, weathering and a wide range of solvents due to unsaturated nature of NR chains and its non-polarity. In efforts to extend its use, there have been various methods developed in order to modify its properties such as hydrochlorinated NR (Nghia Onoe, Yamamoto, and Kawahara, 2008), epoxidized NR (Thongpin et al., 2006) and grafted NR (Kumar and Kothandaraman, 2008). One of the most practical modification methods is grafting the second polymer onto the NR backbone. Reactions involving free radicals have been the most widely applied in grafting processes, and such reactions have been used with a wide range of polymers and monomers (Kumar and Kothandaraman, 2008; Lehrle and Willist, 1997; Oliveira et al., 2005). The grafting of monomers onto NR chains can be represented by the following mechanism.

Initiation:

Attacking monomer: $RO\cdot + M \longrightarrow M_n\cdot$

Attacking rubber: $RO\cdot + NR\text{-}H \longrightarrow NR\cdot + ROH$

Reinitiation: $NR\cdot + M \longrightarrow NR\text{-}M_n\cdot$

Propagation:

Propagation of free polymerization: $M_n\cdot + M \longrightarrow M_{n+1}\cdot$

Propagation of graft polymerization: $NR\text{-}M_n\cdot + M \longrightarrow NR\text{-}M_{n+1}\cdot$

Chain transfer to macromolecules:

Transfer to monomer: $NR\text{-}M_n\cdot + M \longrightarrow M\cdot + NR\text{-}M_n$

Transfer to rubber: $NR\text{-}M_n\cdot + NR\text{-}H \longrightarrow NR\cdot + NR\text{-}M_nH$

$M_n\cdot + NR\text{-}H \longrightarrow NR\cdot + M_nH$

Transfer to chain-transfer agent: $M_n\cdot + A \longrightarrow A\cdot + M_n$

$NR\text{-}M_n\cdot + A \longrightarrow A\cdot + NR\text{-}M_nH$

Termination by combination:

$M_n\cdot + M_m\cdot \longrightarrow M_{n+m}$

$NR\text{-}M_n\cdot + NR\text{-}M_m\cdot \longrightarrow NR\text{-}M_{n+m}\text{-}NR$

$NR\text{-}M_n\cdot + M_m\cdot \longrightarrow NR\text{-}M_{n+m}$

Here, $RO\cdot$ represents the initiating free radical. M and $M_n\cdot$ are the monomer and monomer radical. NR and $NR\cdot$ and $NR\text{-}M_m\cdot$ are polyisoprene, polyisoprene radical and grafted polyisoprene. A and $A\cdot$ are chain transfer reagent and chain transfer reagent radical.

Grafting is mostly carried out using vinyl monomers like methyl methacrylate (MMA) and styrene (Charmondusit et al., 1998). The quantities of grafted monomer on natural rubber molecules are affected by various parameters such as monomer and initiator concentrations, reaction time and reaction temperature.

Oliveira et al. (2005) investigated the grafting efficiency of dimethylaminoethylmethacrylate (DMAEMA) grafted onto natural rubber (NR). The results from ^{1}H-NMR spectroscopy showed that no detectable grafting between NR and DMAEMA occurred when 10 wt% of DMAEMA were used. On the other hand, the amount of grafting increased to a significant amount when NR was grafted with 30% DMAEMA.

Nakason et al. (2004) studied the grafting of maleic anhydride (MA) onto natural rubber in a toluene solution. It was found that quantities of the grafted MA on NR molecules increased with increasing monomer and initiator concentrations. An increase of reaction time and reaction temperature also caused the increasing level of grafted MA. However, increasing initiator concentration (>3.0 phr), reaction temperature (>80^{o}C) and reaction time (>2.0 h) caused the presence and increasing level of the gel fraction in the graft copolymer.

Nakason et al. (2003) investigated the preparation of graft copolymers from deproteinized (DPNR) and high ammonia concentrated (HA) natural rubber latex with methyl methacrylate. The results showed that a larger quantity of grafted poly(methyl methacrylate), PMMA, a larger average particle size and a fewer free natural rubber molecules were observed in the grafting system with DPNR. The levels of grafted PMMA for the graft copolymer obtained from DPNR were higher than those of the graft copolymer of HA. It was believed that proteins played a significant role in free-radical polymerization. This could be because the free-radical species may be terminated by proteins during graft copolymerization.

Charmondusit et al. (1998) investigated grafting of methyl methacrylate and styrene onto natural rubber by core-shell emulsion polymerization to use as an impact modifier for polyvinyl chloride (PVC). The optimum condition of graft copolymerization was found to be at 100 parts by weight of monomer per 100 parts by weight of NR latex, 1.5 parts by weight of emulsifier, 1.5 parts by weight of initiator and at a temperature of 70^{o}C for 8 h. The grafted NR product could be used as an impact modifier for PVC resin to form PVC/grafted NR product blends by mechanical blending and compression molding. The good mechanical properties were obtained at 10 and 15 phr of the grafted NR product.

Suriyachi et al. (2004) grafted glycidyl methacrylate (GMA) and styrene (ST) onto natural rubber latex by emulsion polymerization using cumene hydroperoxide and tetraethylene pentamine as a redox initiator. The effects of initiator and monomer concentration, reaction temperature and time on grafting efficiency and monomer conversion were investigated. The appropriate condition for graft copolymerization was found to be an initiator concentration of 2.5 phr, a monomer concentration of 100 phr and a reaction temperature of 60^{o}C for 10 h. The conversion under this condition was 69.3% and the grafting efficiency was 69.3%. The result from transmission electron microscopy showed that grafted natural rubber had the core shell configuration with complete closed shells of ST and GMA copolymer around the cores of each natural rubber particle. The grafted natural rubber product (NR-g-ST/GMA) was used as a compatibilizer for natural rubber/polymethyl methacrylate, PMMA, blends. The fracture surfaces of natural rubber/PMMA blends showed good interfacial adhesion upon the addition of grafted natural rubber.

George, Britton, and Sebastian (2003) studied graft copolymerization of methyl methacrylate, MMA, onto natural rubber in latex by gamma irradiation for improving the mechanical properties of the dry film. The result showed that modulus of the films was improved with increasing MMA content but tensile strength was reduced. Nevertheless, high modulus without much reduction in tensile strength can be achieved if the MMA content was 50-60 phr.

Derouet et al. (2009) prepared graft copolymers of natural rubber/poly(dimethyl(acryloyloxymethyl)phosphonate), NR-g-PDMAMP, and natural rubber/poly(dimethyl(methacryloyloxyethyl)phosphonate), NR-g-PDMMEP, from photopolymerization in latex medium. The effects of monomer concentration on monomer conversion and grafting rate were studied. It was found that conversion and grafting rate increased with increasing monomer concentration and reaction time.

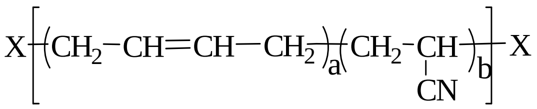
2.5 Rubber-toughened epoxy resins

2.5.1 Types of rubber modifiers

Types of rubber which have been considered and studied with a view to rubber modification of epoxies are listed below:

2.5.1.1 Reactive butadiene-acrylonitrile rubbers

Butadiene-acrylonitrile rubbers comprise a relatively low molecular weight backbone of butadiene and acrylonitrile groups with reactive groups in the terminal position which can be either amine or carboxyl group as shown in Figure 2.7



$$X\!-\!\left[(CH_2\!-\!CH\!=\!CH\!-\!CH_2)_a(CH_2\!-\!\underset{\displaystyle CN}{CH})_b\right]\!-\!X$$

Figure 2.7 Molecular formula of butadiene-acrylonitrile rubber (Collyer, 1994).

2.5.1.2 Reactive acrylate elastomers

Ratna (2001) used carboxyl-terminated poly(2-ethyl hexyl acrylate), CTPEHA (Figure 2.8), to improve toughness of epoxy networks.

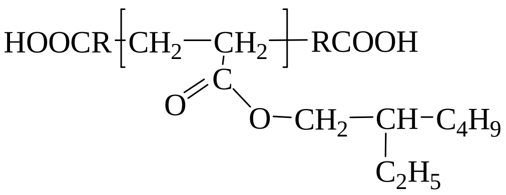


Figure 2.8 Chemical structure of CTPEHA (Ratna, 2001).

Kong et al. (2006) used the acrylate liquid rubber (Figure 2.9) to toughen bisphenol A diglycidyl ether epoxy resins with triethanolamine as hardener.

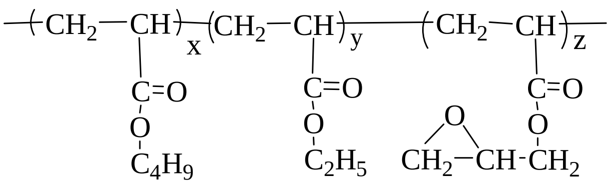


Figure 2.9 Molecular formula of acrylate liquid rubber containing pendant epoxy group (Kong et al., 2006).

2.5.1.3 Polysiloxanes

Rutnakornpituk (2005) found that the fracture toughness properties of the epoxy-novolac networks were improved with the statistical epoxidized polycyanopropylmethylsiloxane-co-polydimethylsiloxanes (PCPMS-co-PDMS). Figure 2.10 shows the chemical structure of PCPMS-co-PDMS.

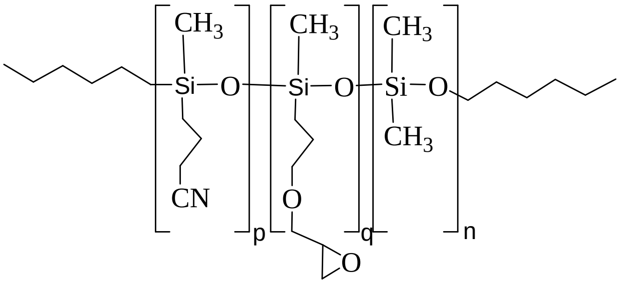


Figure 2.10 Chemical structure of PCPMS-co-PDMS (Rutnakornpituk, 2005).

2.5.1.4 Reactive polybutadiene rubbers

Ramos et al. (2005) used hydroxyl-terminated polybutadiene, HTPB (Figure 2.11) as impact modifier for epoxy resin.

$$HO\left[\left(CH_2CH{=}CHCH_2\right)\right]_y OH$$

Figure 2.11 Chemical structure of HTPB (Ramos et al., 2005).

2.5.1.5 Modified natural rubber

Chuayjuljit et al. (2006) prepared epoxidized natural rubber, ENR (Figure 2.12) using *in sit*u epoxidation technique. ENR product was applied as impact modifier for epoxy resin.

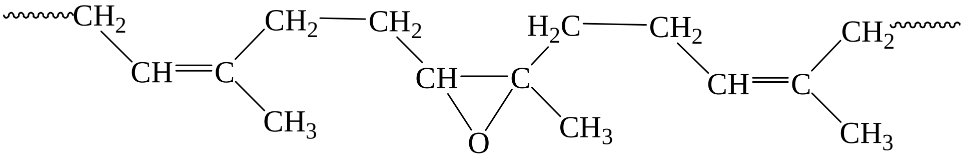


Figure 2.12 Chemical structure of ENR (Chuayjuljit et al., 2006).

Kumar and Kothandaraman (2008) modified epoxy resin with maleated depolymerized natural rubber, MDPR (Figure 2.13).

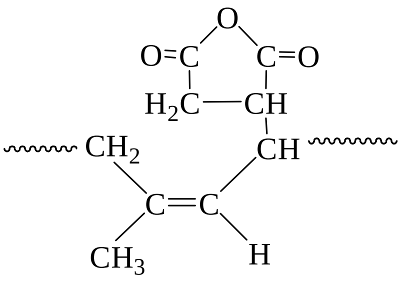


Figure 2.13 Chemical structure of MDPR (Kumar and Kothandaraman, 2008).

2.5.2 Toughening mechanism

A number of quite different toughening mechanisms in rubber-toughened epoxy resins have been proposed. These include crazing, shear yielding and rubber cavitation as shown in Figure 2.14-2.16, respectively.

Barcia, Thiago, and Soares (2003) studied impact behavior of block copolymer of polybutadiene modified bisphenol A diglycidyl ether (DGEBA) based epoxy resin. They observed the impact behavior of the toughened networks using scanning electron microscope. They found that the toughening mechanism was related to the cavitation in the rubber particles dispersed inside the epoxy matrix. They also suggested that, according to Bucknall and Smith's theory, the rubber particles initiate the formation of crazes and control their growth. Moreover, they explained that there is the flexibility effect. The flexibility is caused by the presence of dissolved rubber inside the epoxy matrix. Similar result has been reported by Saadati et al. (2005).

Pearson and Yee (1991) observed the influence of particle size and particle size distribution of rubber on toughening mechanisms in rubber-modified epoxies. They found that the toughness was increased by cavitations-induced shear banding. Similar behavior has also been reported in the study on the modification of epoxy resins with acrylate liquid rubber containing pendant epoxy groups (Kong et al., 2006). Kong et al. (2006) illustrated that the rubber globular particles dispersed in the connected epoxy resin phase acted as center for dissipation of mechanical energy by cavitations and shear yielding. The results could be proved by the existence of cavitations of rubber particles and corresponding stress whitened zone around rubber particles.

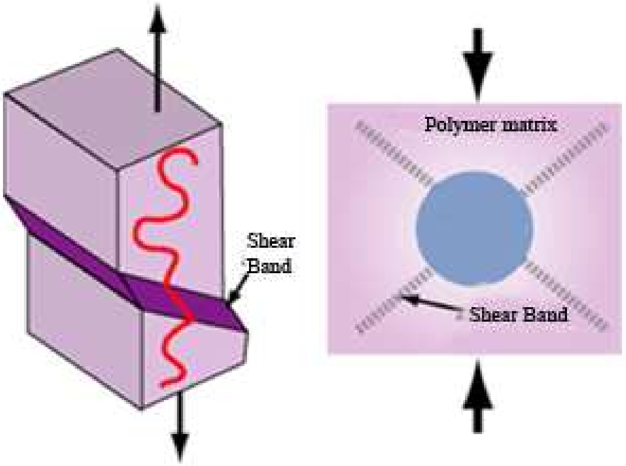


Figure 2.14 Schematic diagram of shear yielding (SpecialChem Innovation & Soultions, 2008).

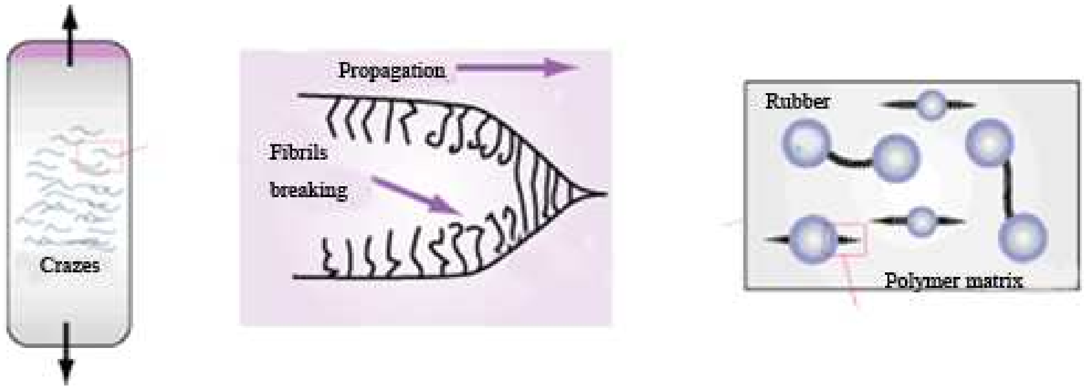


Figure 2.15 Schematic diagram of crazing (SpecialChem Innovation & Soultions, 2008).

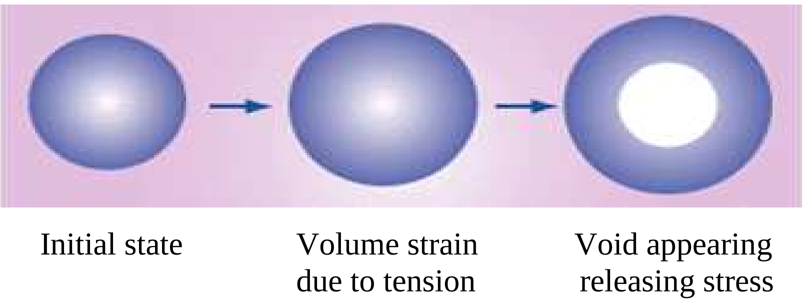


Figure 2.16 Schematic diagram showing cavitation of a rubber particle (SpecialChem Innovation & Soultions, 2008).

In addition, Ratna (2001) used scanning electron microscopy to observe toughening mechanism of carboxyl-terminated poly(2-ethyl hexyl acylate), CTPEHA, modified epoxy resin. SEM micrograph showed the broken rubber particles and stress whitening zone. The researcher explained that stress whitening is due to the scattering of visible light from the layer of the scattering centers which in this case are voids. The generation of the voids is due to the cavitation of rubber particles.

Thomas et al. (2008) also reported similar results for hydroxyl terminated polybutadiene, HTPB, modified epoxy resin.

In 1996, Bagheri and Pearson studied rubber-modified epoxy resin. The rubbers used are hollow latex particles (HLP) with a styrene-acrylic shell, carboxyl terminated butadiene acrylonitrile copolymer (CTBN) and core-shell latex particle comprised of a methacrylated butadiene-styrene copolymer with acid functionality in poly(methyl methacrylate) (PMMA) shell (MBS-COOH). They observed the crack tip of modified epoxies using transmission optical microscopy. They found shear yielding in all cases. However, shear bands are much finer in case of epoxies toughened by smaller size modifiers.

Chikhi et al. (2002) found that toughness of DGEBA was improved by adding amine-terminated butadiene acrylonitrile. An increase of toughness was due to some cavitation of the rubber particles accompanied by stress whitening zones developed on the fracture surface of the modified epoxy. This stress whitening effect was related to the local plastic deformation at the crack tip. Furthermore, the cavitation was followed by the onset of shear localization process. Similar results have been reported elsewhere (Ratna, Banthia, and Deb, 2000).

Recently, Ratna and Banthia (2007) employed reactive acrylic liquid rubber containing terminal and pendant carboxyl groups as a modifier for epoxy resin. The results illustrated that toughness of epoxy increased with increasing functionality of the liquid rubber. They suggested that an increase in functionality of rubber led to higher matrix-particle adhesion which resulted in rubber cavitation and plastic deformation.

Kumar and Kothandaraman (2008) showed shear banding between maleated depolymerized natural rubber particle in epoxy matrix, which advocated appreciable matrix shear yielding and plastic deformation over a large volume of rubber. This attributed to the improvement of impact strength value of the blends.

2.5.3 Factors affecting toughness of rubber-toughened epoxy resins

Many investigations conducted on epoxies have indicated several factors likely to influence toughness of rubber-toughened epoxy resins. These include rubber concentrations, molecular weight, particle size, inter-particle distance and cure conditions.

Bagheri and Pearson (1996, 2000) studied toughness of rubber-toughened epoxy resins with CTBN and core-shell latex particles modifiers. It was found that, at the same particle size, the inter-particle distance decreased when rubber volume fraction was increased. This led to an increase of fracture toughness. At the same volume fraction, the smaller particles gave lower inter-particle distance and higher fracture toughness.

Ratna et al. (2000) investigated the effect of molecular weights of carboxyl-terminated poly(2-ethylhexyl acrylate), CTPEHA, on impact energy of CTPEHA/epoxy blends. CTPEHA with number average molecular weights, M_n, in the range of 3500-7000 g/mol performed almost equally toughening efficiency. However, the liquid rubber with M_n = 9500 g/mol, was found to be ineffective in toughening epoxy. This could be because of the formation of large agglomerates.

Ratna (2001) studied relationship between impact behavior and initial curing condition of carboxyl-terminated poly(2-ethyl hexyl acylate), CTPEHA, liquid rubber-modified epoxy resins. The impact strength of the modified networks slowly increased with an increase in initial cure temperature up to 140^{o}C and decreased with a further increase in initial cure temperature. Similar behavior has been also reported in hydroxyl terminated polybutadiene rubber-modified epoxy system (Thomas et al., 2008).

Several reports have shown an influence of rubber concentration on toughness of epoxies. Ratna (2001) illustrated the relationship between the concentration of CTPEHA and notched Izod impact strength per unit width of the specimen. The impact strength of the modified epoxy samples was higher than that of the unmodified epoxy. The modified network containing 10 phr showed maximum impact strength of 25.6 J/m which is about 60% higher than the neat epoxy (16.3 J/m).

Chikhi et al. (2002) found that the toughness of amine-terminated butadiene acrylonitrile, ATBN, modified epoxy resin increased with an increase of ATBN content up to 12.5 phr in comparison with that of unfilled resin.

Moreover, it is well known that the reactivity and selectivity of the elastomer play an important role in the process. Functional groups must present in the chain of the rubber in order to promote the formation of chemical bonds with the epoxy matrix, which are necessary for an efficient stress transfer between the rubber particles and the matrix.

Ramos et al. (2005) evaluated and compared the use of carboxyl-terminated butadiene acrylonitrile copolymer (CTBN) and hydroxyl-terminated polybutadiene (HTPB) as impact modifiers for epoxy resin. They found that CTBN led to higher impact strength than HTPB. The results from rubber particle size observation revealed that the materials modified with CTBN showed CTBN particle size was between 1-4 μm. On the other hand, HTPB modified epoxy resin showed large difference in rubber particle size that ranges from 10 to 50 μm. A lower in toughening efficiency of HTPB could be because the interaction between the HTPB particle and matrix was not satisfactory.

Generally, carboxyl termination has usually been shown to exert a greater toughening effect than most other functionalities including phenol, epoxy, hydroxyl and mercaptan (Table 2.3).

Table 2.3 Effect of terminal functionality on the toughening ability of butadiene-acrylonitrile elastomer (Collyer, 1994).

Elastomer	**Functionality**	**Fracture energy (kJ/m^2)**
CTBN	Carboxyl	2.8
PTBN	Phenol	2.6-3.0
ETBN	Epoxy	1.8-2.5
HTBN	Hydroxyl	0.9-2.6
MTBN	Mercaptan	0.2-0.4

Recently, Kumar and Kothandaraman (2008) studied grafting maleic anhydride onto depolymerized natural rubber. The maleated depolymerized natural rubber (MDPR) obtained was used as a minor phase for epoxy matrix. The results showed that the impact strength values of the 1 and 2 phr MDPR/epoxy blends were higher than that of the unmodified epoxy.

CHAPTER III

EXPERMENTAL

3.1 Materials and chemical reagents

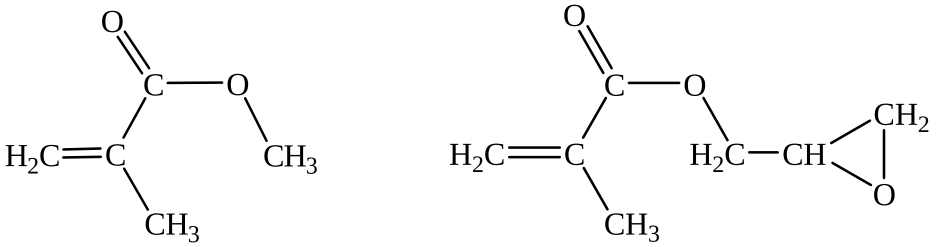
High ammonia natural rubber latex concentrates were supplied by Thai Hua Rubber Public Co., Ltd. (Udornthani, northeastern region of Thailand). The specification of high ammonia natural rubber latex concentrates is shown in Table 3.1.

Table 3.1 Specification of high ammonia natural rubber latex concentrates.

Specification	**Content**
1. Total solids content, %	61.23
2. Dry rubber content (DRC), %	60.09
3. Non-rubber solid content, %	1.14
4. NH_3 content (on total weight), %	0.60
5. NH_3 content (on water phased), %	1.55
6. pH value	10.48
7. Potassium hydroxide number	0.52
8. Volatile fatty acids number	0.04
9. Latex mechanical stability time, sec	330
10. Mg^{2+} (on solid), ppm	39.35

Deionized (DI) water, methyl ethyl ketone ($CH_3CH_2COCH_3$, Carlo Erba, 99.5%), potassium persulfate ($K_2S_2O_8$, Aldrich, 99%), potassium hydroxide (KOH, Aldrich, 85%) and high ammonia natural rubber were used in the preparations of depolymerized natural rubber (DNR). Calcium chloride ($CaCl_2$, Carlo Erba, 92%) was employed to coagulate DNR. n-Hexane ($CH_3(CH_2)_4CH_3$, Carlo Erba, 95%) was used to dissolve DNR. Methyl alcohol (CH_3OH, Carlo Erba, 99.9%) was applied to precipitate DNR.

Toluene ($C_6H_5CH_3$, Carlo Erba, 99.5%) was used as a solvent for grafting DNR. Methyl methacrylate ($C_5H_8O_2$, Fluka, 99%) and glycidyl methacrylate ($C_7H_{10}O_3$, Aldrich, 97%) were used as the monomers for grafting DNR. The chemical structures of the monomers are shown in Figure 3.1.

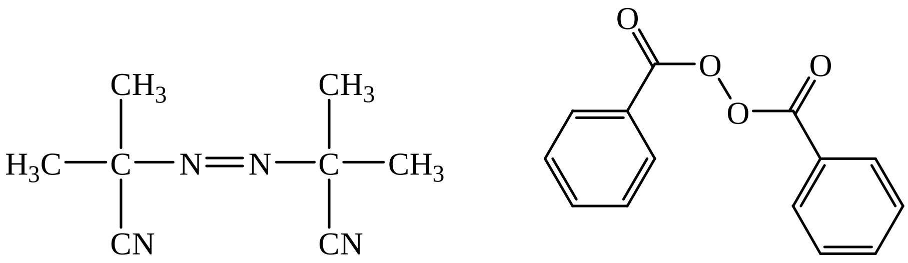


Glycidyl methacrylate (GMA)

Methyl methacrylate (MMA)

Figure 3.1 Chemical structures of glycidyl methacrylate and methyl methacrylate.

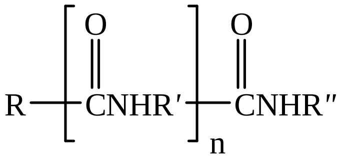
Sodium hydroxide (NaOH, Carlo Erba, 97%) was used to remove the inhibitor. Initiator for grafting process was azo-bis-isobutyronitrile (AIBN) and benzoyl peroxide (BPO). The chemical structures of the initiators are shown in Figure 3.2.



Azo-bis-isobutyronitrile (AIBN) Benzoyl peroxide (BPO)

Figure 3.2 Chemical structures of azo-bis-isobutyronitrile and benzoyl peroxide.

Acetone ($C_3H_6O_6$, 99.8%) was applied to precipitate grafted depolymerized natural rubber (GDNR). Bisphenol-A based epoxy resin (Epiclon 850) with epoxide equivalent weight 184-194 g/equivalent and polyamide (Luckamide GL 120) were supplied by Siam Chemical Industry Co., Ltd. The chemical structure of polyamide is shown in Figure 3.3. Fiber glass (Chopventager HP3610) with 3 mm in length was supplied by Behn Meyer Chemical (T) Co., Ltd.



$$R\!-\!\left[\overset{\displaystyle O}{\overset{\|}{C}}NHR'\right]_n\!-\!\overset{\displaystyle O}{\overset{\|}{C}}NHR''$$

Figure 3.3 Chemical structure of polyamide.

3.2 Experimental

3.2.1 Preparation of depolymerized natural rubber

61.23% Total solid content natural rubber latex was diluted by deionized water to a concentration of 5 wt% based on rubber content in a 1 liter reaction flask, followed by the addition of $CH_3CH_2COCH_3$ and $K_2S_2O_8$ in an amount of 4 v% of total volume and 2 wt% based on the rubber content, respectively. The pH of latex was adjusted to about 9-10 with 10 wt% aqueous KOH solution. Then, the reaction mixture was mechanically stirred with a speed of 200 revolutions per minute (rpm) at 70°C in water bath for 24 h under a flowing air. At the end of reaction, the reaction mixture was coagulated by 1 wt% aqueous $CaCl_2$ solution. The coagulated substance was dissolved in hexane and stirred with magnetic bar for 3 h. Then, resulting solution was stood overnight and filtered with vacuum buchner. The filtrate was purified two times by the re-precipitation method using methanol, followed by vacuum drying at 40^oC until weight is constant.

3.2.2 Preparation of grafted depolymerized natural rubber

To remove inhibitor, methyl methacrylate (MMA) monomer was washed twice with 2 wt/v% NaOH solutions (ratio of mixture 1/1 v/v%) in a separating funnel. Then, monomer was cleaned three times with DI water to remove residual sodium hydroxide. After that, anhydrous $CaCl_2$ was added overnight into monomer to remove moisture in a refrigerator. Next, the monomer was filtered through a filter paper to separate $CaCl_2$. The inhibitor-free MMA monomer was further used in grafting process. GMA monomer was used as received.

Grafted depolymerized natural rubber (GDNR) was synthesized in a solution state. In a typical solution-grafting process, DNR was dissolved in toluene (1 g of DNR:10 ml of solvent) and heated to 80°C with stirring at about 200 rpm under a flowing nitrogen atmosphere. After completing dissolution of DNR, the monomer mixture of MMA/GMA (90/10 wt/wt%) was added and stirred for 10 min. The addition of free radical initiator was followed. The reaction was continued for 2 h. At the end of reaction, the graft copolymer was precipitated by adding acetone at room temperature. After thoroughly washing with acetone five times, the graft copolymer was kept to a vacuum oven at 40°C until weight is constant. The amount of each variable reactant added to the reaction mixtures is shown in Table 3.2. In each reaction, DNR 5 g and toluene 50 ml were used.

Table 3.2 Amount of each variable reactant added to the reaction mixtures.

GDNR	**MMA (g)**	**GMA (g)**	**AIBN (g)**	**BPO (g)**
20_1AIBN	0.90	0.10	0.05	-
20_2AIBN	0.90	0.10	0.10	-
20_3AIBN	0.90	0.10	0.15	-
30_1AIBN	1.35	0.15	0.05	-
30_2AIBN	1.35	0.15	0.10	-
30_3AIBN	1.35	0.15	0.15	-
50_1AIBN	2.25	0.25	0.05	-
50_2AIBN	2.25	0.25	0.10	-
50_3AIBN	2.25	0.25	0.15	-
75_1AIBN	3.38	0.38	0.05	-
75_2AIBN	3.38	0.38	0.10	-
75_3AIBN	3.38	0.38	0.15	-
50_1BPO	2.25	0.25	-	0.07
50_2BPO	2.25	0.25	-	0.13
50_3BPO	2.25	0.25	-	0.20

The effect of types of initiator was compared between AIBN and BPO at 50 phr of monomer mixture. Furthermore, effects of monomer and initiator concentration on the degree of graftization of DNR grafted with MMA/GMA were studied. The amounts of initiator were varied from 1 to 3% based on DNR content. The amounts of monomer mixture was varied from 20 to 75 parts per hundred (phr) of DNR.

The nomenclature used to describe the GDNR is demonstrated by considering 20_1AIBN. The ‘20’ corresponds to the amount of monomer used in part per hundred of DNR (phr). The following digit represents the percentage of initiator based on rubber content. The ‘AIBN’ is the type of initiator used to prepare GDNR. Thus, the 20_1AIBN defines GDNR prepared using 20 phr of monomer mixture, 1 percent of initiator based on rubber content and AIBN was used as an initiator.

Grafting reaction that gave GDNR with suitable degree of graftization and proper characteristic was scaled up to prepare GDNR for blending with epoxy resin. For each large scale reaction, DNR 15 g and toluene 150 ml were used. The amount of each variable reactant added to the reaction mixtures is shown in Table 3.3.

Table 3.3 Amount of each variable reactant added to the large scale reaction mixtures.

GDNR	**MMA (g)**	**GMA (g)**	**AIBN (g)**
20_2AIBN(L)	2.70	0.30	0.30
30_2AIBN(L)	4.05	0.45	0.30
50_2AIBN(L)	6.75	0.75	0.30

3.2.3 Preparation of rubber/epoxy resin blends

The rubber (DNR or GDNR) was dissolved completely in epoxy resin at 80^{o}C using mechanical stirrer at a speed of 500 rpm for 1 h. The epoxy resin and rubber mixtures were allowed to reach 60^{o}C. Next, 40 phr of polyamide (Luckamide GL 120) were added and stirred at a speed of 200 rpm for 3 min. Thereafter, the blends were poured into a steel rectangular mould previously coated with releasing agent. Then the mixture was degassed for 15 min in vacuum dessicator and cured at room temperature for 4 h. After that, each specimen was cut and polished with sandpaper. Finally, the specimen was post-cured at 120°C for 2 h in a mechanical convection oven. The composition of (G)DNR/epoxy blends are shown in Table 3.4.

Table 3.4 Composition of (G)DNR/epoxy resin blends.

Designation	Epoxy resin (g)	Hardener (g)	DNR (g)	GDNR (g)
Neat epoxy	100	40	-	-
0.5_DNR	100	40	0.5	-
1_DNR	100	40	1.0	-
2_DNR	100	40	2.0	-
3_DNR	100	40	3.0	-
1_20_2AIBN(L)	100	40	-	1.0
1_30_2AIBN(L)	100	40	-	1.0
1_50_2AIBN(L)	100	40	-	1.0

3.2.4 Preparation of rubber/fiber glass/epoxy composites

Fiber glasses (GF) were thermal treated at 500^{o}C for 3 h in a muffle furnace before use. The rubber (1 phr of DNR or GDNR) was dissolved completely in epoxy resin at 80^{o}C using mechanical stirrer at a speed of 500 rpm for 1 h. After that, 5 wt% GF were added and stirred at a speed of 200 rpm for 5 min. Then the mixtures were allowed to reach 60^{o}C. Next, 40 phr of polyamide (Luckamide GL 120) were added and stirred at a speed of 200 rpm for 3 min. Thereafter, the blends were poured into a steel rectangular mould previously coated with releasing agent. Then the mixture was degassed for 15 min in vacuum dessicator and cured at room temperature for 4 h. After that, each specimen was cut and polished with sandpaper. Finally, the specimen was post-cured at 120°C for 2 h in a mechanical convection oven. The composition of (G)DNR/fiber glass/epoxy composites are shown in Table 3.5.

Table 3.5 Composition of (G)DNR/fiber glass/epoxy composites.

Designation	**Epoxy resin (g)**	**Hardener (g)**	**Fiber glass (g)**	**DNR (g)**	**GDNR (g)**
Neat epoxy	100	40	-	-	-
5% GF	100	40	5	-	-
1_DNR_5% GF	100	40	5	1	-
1_30_2AIBN(L)_5% GF	100	40	5	-	1

3.2.5 Material characterization

3.2.5.1 Molecular weight and molecular structure of rubber

In order to determine molecular structure of NR, DNR and GDNR, nuclear magnetic resonance spectroscopy in a 300 MHz spectrometer (Varian, Inova 300) at 30°C with deuterated chloroform as a solvent was used. The concentration of the rubber in deuterated chloroform solution was 1-3 wt/v%. Tetramethylsilane (TMS) was used as internal reference and chemical shifts were reported in ppm.

The molecular weight and molecular weight distribution of NR, DNR and GDNR were investigated by gel permeation chromatography (GPC). The GPC instrument was equipped with universal styrene-divinylbenzene copolymer columns (PLgel Mixed-C, 300×7.5 mm, 5µm) and differential refractometer detector (RI-G1362A). Temperature of the column and the detector was maintained at 40ºC and 35ºC, respectively. The molecular weight of the samples was obtained from calibration curves using polystyrene standards (Shodek standard). Chloroform was used as the mobile phase at a flow rate of 1 ml/min. The concentration of the rubber in chloroform solution was 0.1 wt/v%. The solution was filtered through a 0.45 µm polyamide filter paper prior to measurement.

3.2.5.2 Mechanical properties

Notched Izod impact strength of the neat epoxy resin, the rubber/epoxy blends and rubber/fiber glass/epoxy composites was tested according to the ASTM D 256, method A, using a basic pendulum impact tester (Atlas model BPI). The total striking impact energy of 2.7 J was assigned at room temperature. The geometry of specimens was 4 mm in thickness, 64 mm in length and 12.7 mm in width. Ten specimens were tested on each material. The impact strength (kJ/m^2) was calculated and reported.

In order to determine flexural properties of the neat epoxy resin, the rubber/epoxy blends, and (G)DNR/fiber glass/epoxy composites, five specimens of each material were examined according to ASTM 790 using a universal testing machine (Instron model 5569) with a load cell of 50 kN, a crosshead speed of 1.66 mm/min and span length of 62.4 mm. The specimens were having a thickness of 4 mm, a width of 15 mm, and the overall length of 87.4 mm. The measurements of flexural modulus, flexural strength, and flexural strain were recorded. The support span (span length) of machine shall be 16 times the depth of the sample. The crosshead speed of machine calculated by the following equation.

$$R = \frac{\mathrm{ZL}^2}{6d}$$

where R = rate of crosshead motion, mm/min

L = support span, mm

d = depth of specimen, mm

Z = rate of straining of the outer fiber, Z shall be equal to 0.01 mm/mm/min

3.2.5.3 Morphological properties

Morphology of the fracture surfaces of the neat epoxy, (G)DNR/epoxy blends, and (G)DNR/ fiber glass/epoxy composites was examined by scanning electron microscope, SEM (JEOL model JSM 6400), employing an accelerating voltage of 10 kV. The sample surfaces were coated with gold before SEM analysis.

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Molecular weight and molecular structure of natural rubber and depolymerized natural rubber

As mentioned in chapter I, the aim of this study is to enhance toughness of epoxy resin by blending with natural rubber (NR). NR is normally a high molecular weight polymer. Therefore, it is difficult to disperse in epoxy resin. To promote initial dispersion of NR in epoxy resin, high molecular weight natural rubber was subjected to depolymerization. Depolymerized natural rubber (DNR) product obtained was a light yellow viscous liquid with sticky character and thoroughly soluble in chloroform. Molecular weight and molecular weight distribution of DNR and dried natural rubber latex, which used as a starting material for DNR production, were determined using gel permeation chromatography. The number average molecular weight, M_n, weight average molecular weight, M_w, and molecular weight distribution, MWD, of NR and DNR are tabulated in Table 4.1.

Table 4.1 Molecular weight and molecular weight distribution of NR and DNR.

Type of rubber	M_n (g/mol)	M_w (g/mol)	MWD
NR	657,720	880,630	1.339
DNR	55,984	135,487	2.420

The results showed that the M_n and M_w of NR were decreased significantly after depolymerization. The molecular weight distribution of DNR was slightly board.

The chemical structures of the NR and DNR were analyzed by proton nuclear magnetic resonance spectroscopy, ^{1}H-NMR. The results shown in Figure 4.1 indicated that DNR obtained had the same chemical shift as NR. The chemical shift at 5.12 ppm was attributed to proton attached to carbon-carbon double bond, unsaturated methyne proton (1H, =CH). The chemical shift at 2.04 ppm was attributed to the methylene protons (4H, $(CH_2)_2$) and the chemical shift at 1.68 ppm was the singlet resonance signal of methyl proton (3H, CH_3).

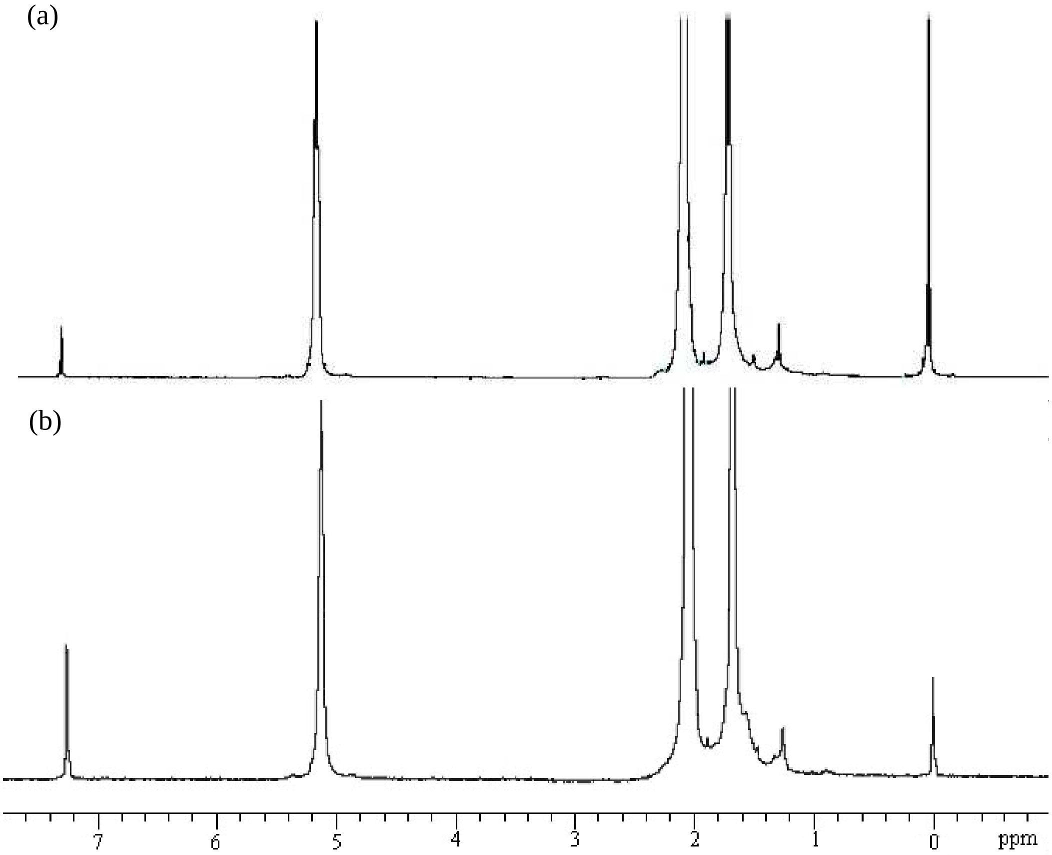


Figure 4.1 ^{1}H-NMR spectrum of DNR (a) and NR (b).

4.2 Characterization of grafted depolymerized natural rubber (GDNR)

4.2.1 Molecular structure of GDNR

In this study, 12 different grafting conditions using azo-bis-isobutyronitrile (AIBN) as an initiator and 3 different grafting conditions using benzoyl peroxide (BPO) as an initiator were performed. GDNR was synthesized in a toluene solution. The monomer mixture of methyl methacrylate/glycidyl methacrylate, MMA/GMA (90/10 wt/wt%) was used. GDNR product which was obtained from each grafting condition was analyzed using ^{1}H-NMR in order to observe the attachment of the monomers onto DNR backbone. The ^{1}H-NMR spectrum of grafted DNR (GDNR) and DNR are compared in Figure 4.2.

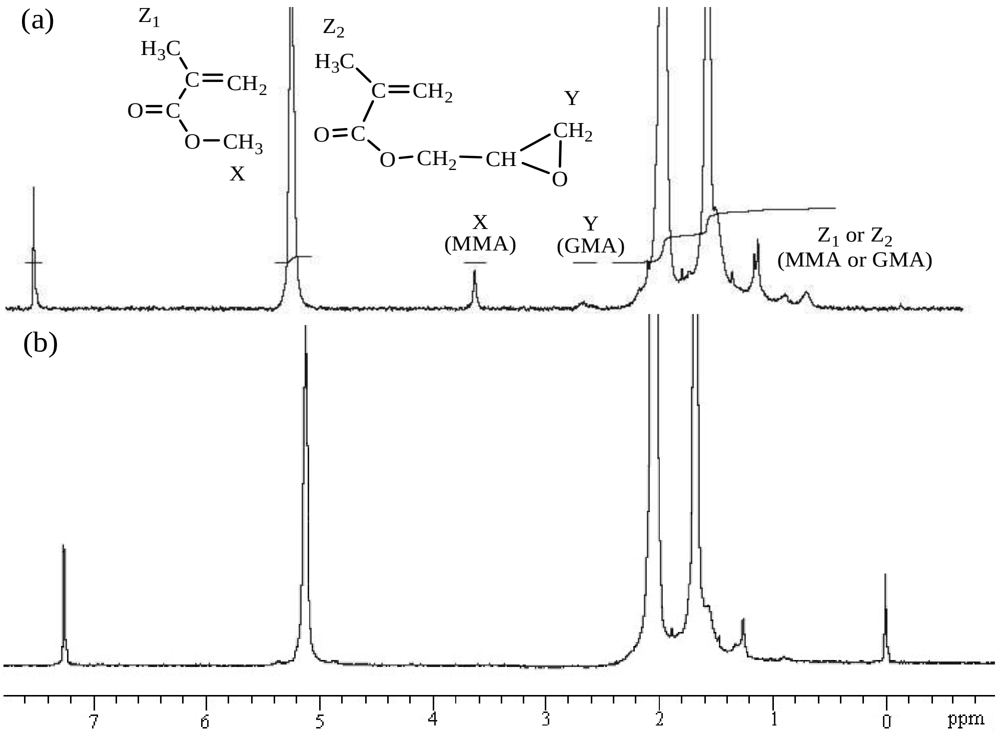


Figure 4.2 ^{1}H-NMR spectrum of GDNR (a) and DNR (b)

As seen in Figure 4.2 (a), the methoxy proton of acrylic group of MMA unit (X) appears at 3.60 ppm. This proved that DNR backbone was successfully grafted with MMA. Furthermore, the chemical shift at 2.65-2.85 ppm might be attributed to the methylene protons of the epoxy group of GMA (Y). Nevertheless, there was rather low signal of GMA attached to DNR backbone. This is not surprising because the amount of GMA used in grafting process was small. The chemical shift at 0.93-1.26 ppm was attributed to saturated methyl proton (α-CH_3) of both MMA (Z_1) (Kongparpkul, Prasassarakich, and Rempel, 2008) and GMA (Z_2) (Espinosa, del-Toro, and Silva, 2001). Therefore, the chemical shifts at 2.65-2.68 and 3.60 ppm which clearly represented the attachment of GMA and MMA onto DNR backbone were chosen for reporting degree of graftization.

In order to show the effect of initiator concentration on molecular structure of GDNR, ^{1}H-NMR spectra of GDNR prepared from 75 phr of monomer mixture using three different AIBN initiator concentrations are illustrated in Figure 4.3. The results showed that GDNR prepared with 2 phr of initiator seemed to show the highest sign of monomer attached to DNR backbone. GDNR prepared from other monomer concentrations (20, 30, and 50 phr) also showed the same trend. This would be later discussed. The results of monomer concentration are shown in Figure 4.4. It could be seen that, at the same initiator concentration, the sign of monomer attached to DNR increased with increasing monomer concentration. Figure 4.5 compared between ^{1}H-NMR spectra of GDNR prepared from AIBN initiator and that prepared from BPO initiator. The BPO initiator tended to give higher level of monomer attached to DNR than AIBN initiator.

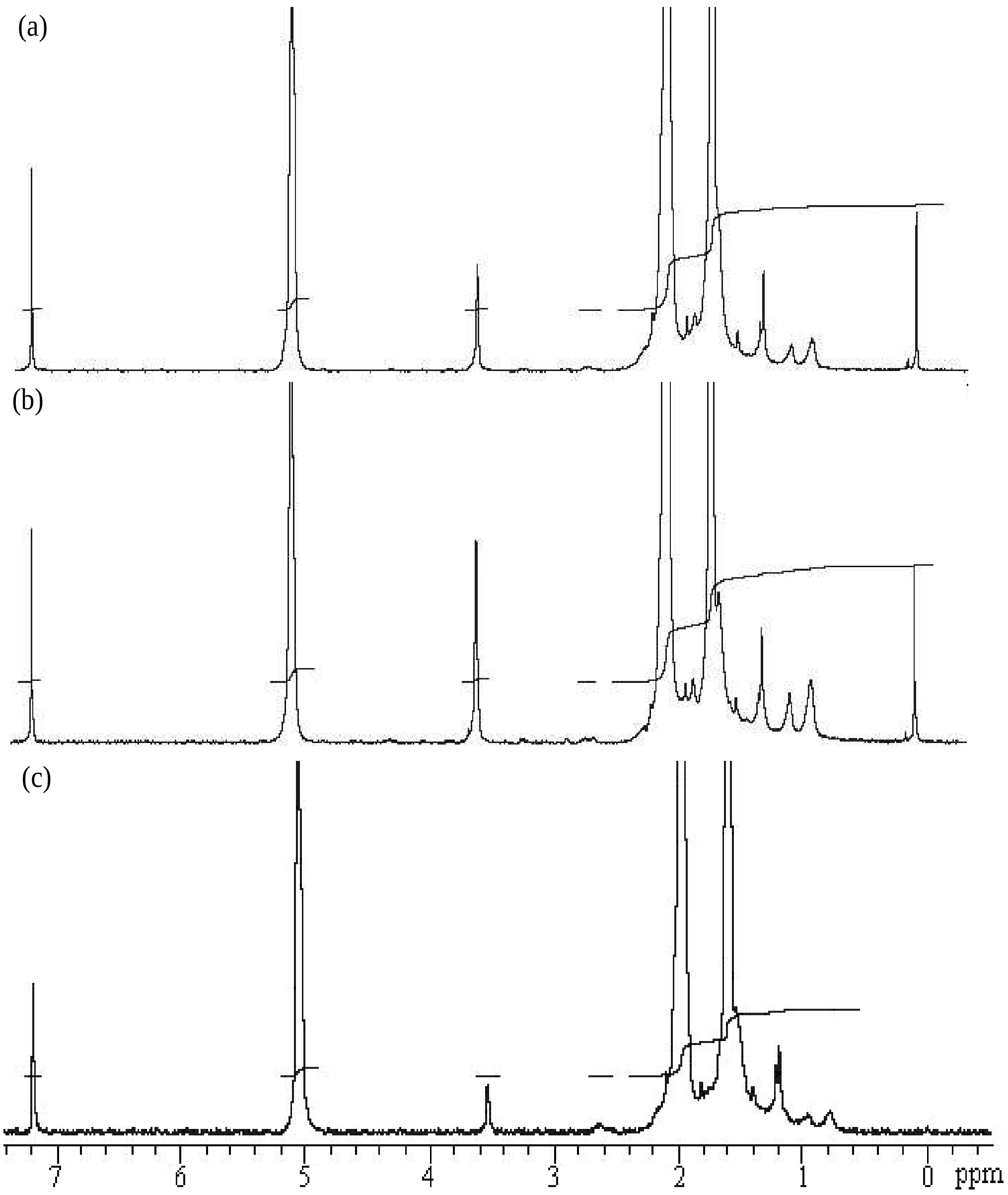


Figure 4.3 ^{1}H-NMR spectra of GDNR; (a) 75_1AIBN, (b) 75_2AIBN and (c) 75_3AIBN.

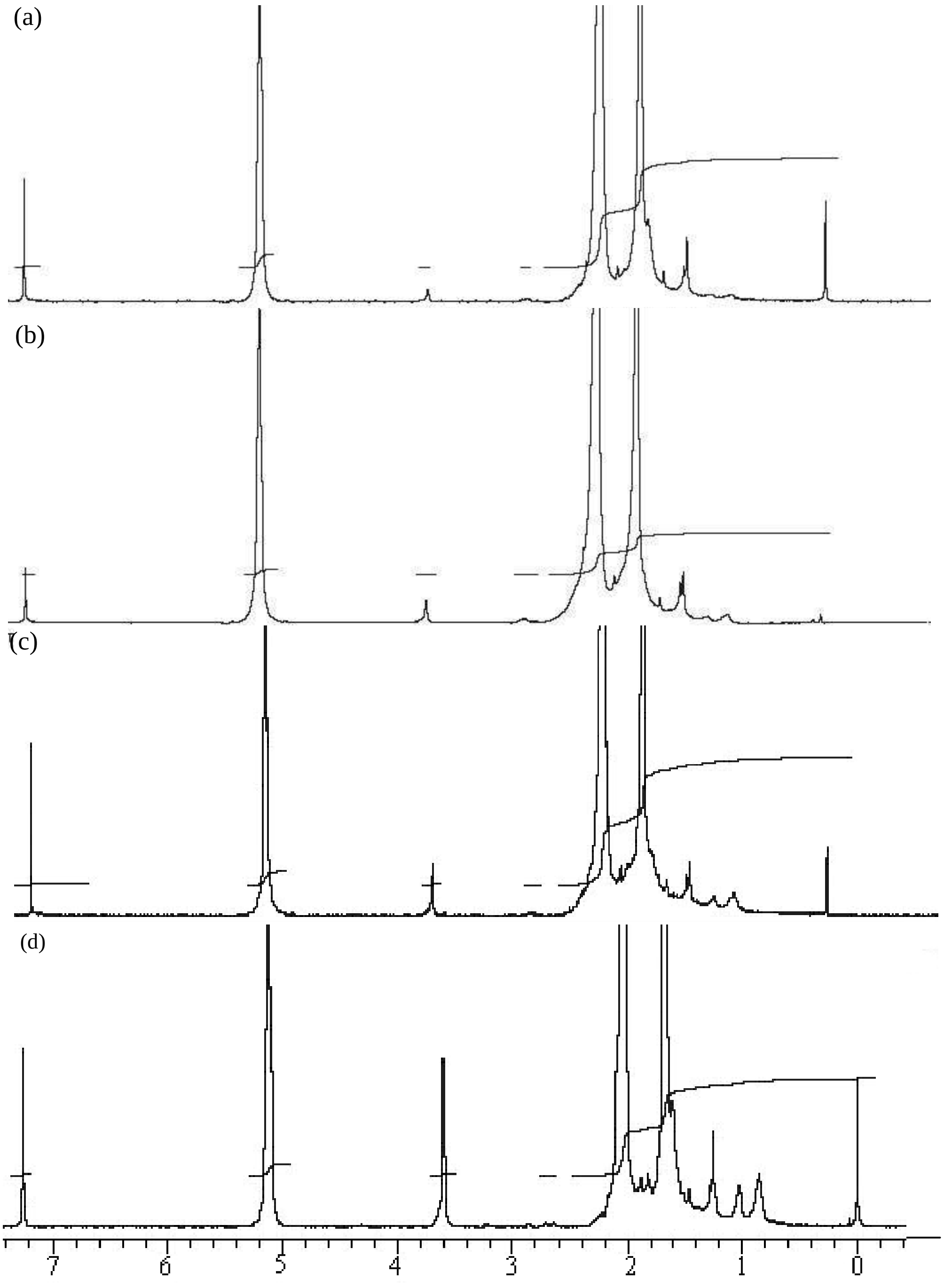


Figure 4.4 ^{1}H-NMR spectra of GDNR; (a) 20_2AIBN, (b) 30_2AIBN, (c) 50_2AIBN and (d) 75_2AIBN.

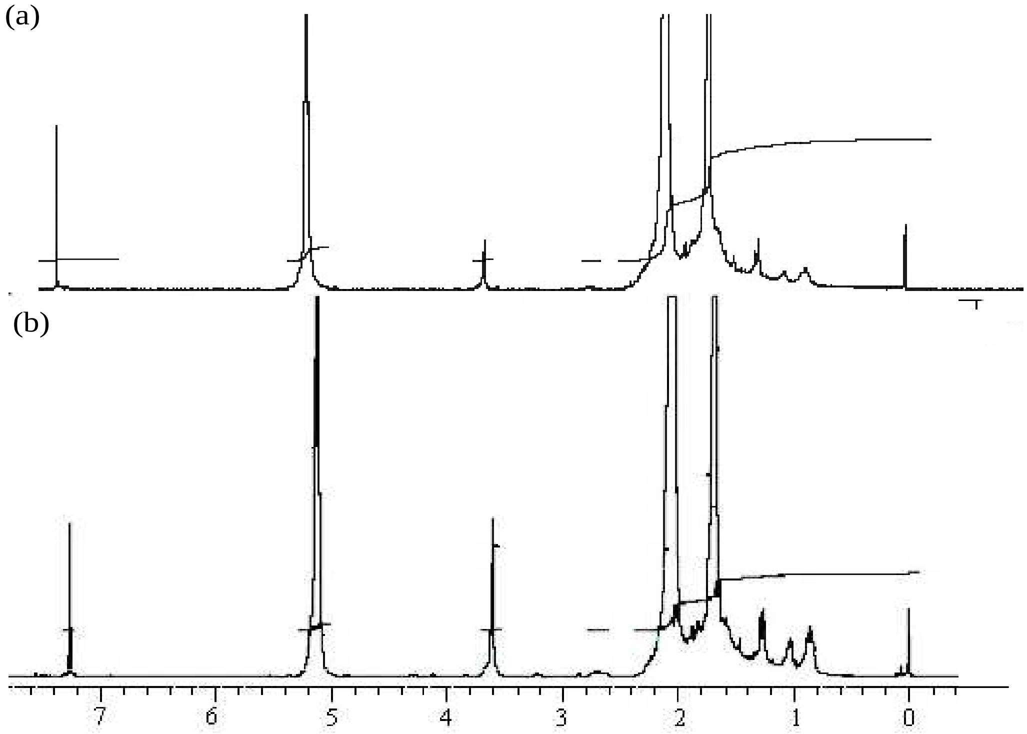


Figure 4.5 ^{1}H-NMR spectra of GDNR; (a) 50_2AIBN and (b) 50_2BPO.

4.2.2 Degree of graftization

In this section, degree of graftization of GDNR prepared from different grafting condition was discussed. The degree of graftization was estimated based on the copolymer composition using the ^{1}H-NMR technique (Arayapranee, Prasassarakich, and Rempel, 2003). Analysis was carried out using a 1-3 wt/v% solution in deuterated chloroform ($CDCl_3$).

From the different signal as shown in Figure 4.6, the amount of MMA per proton (*MMA*), the amount of isoprene per proton (*NR*) and the amount of GMA per proton (*GMA*) were calculated using the following equations:

$$MMA = \frac{A_{\delta 3.60}}{3} \tag{1}$$

$$GMA = \frac{A_{\delta 2.65-2.85}}{2} \tag{2}$$

$$NR = \frac{A_{\delta 5.12}}{1} \tag{3}$$

where $A_{\delta 3.60}$, $A_{\delta 2.65\text{-}2.85}$ and $A_{\delta 5.12}$ are the peak areas corresponding respectively to MMA, GMA and NR.

The fractions of MMA ($F_{MMA\text{-}g}$) and GMA ($F_{GMA\text{-}g}$) in the graft copolymers were calculated by the following equations:

$$F_{MMA-g} = \frac{MMA}{(MMA + GMA)} \tag{4}$$

$$F_{GMA-g} = \frac{GMA}{(MMA + GMA)} \tag{5}$$

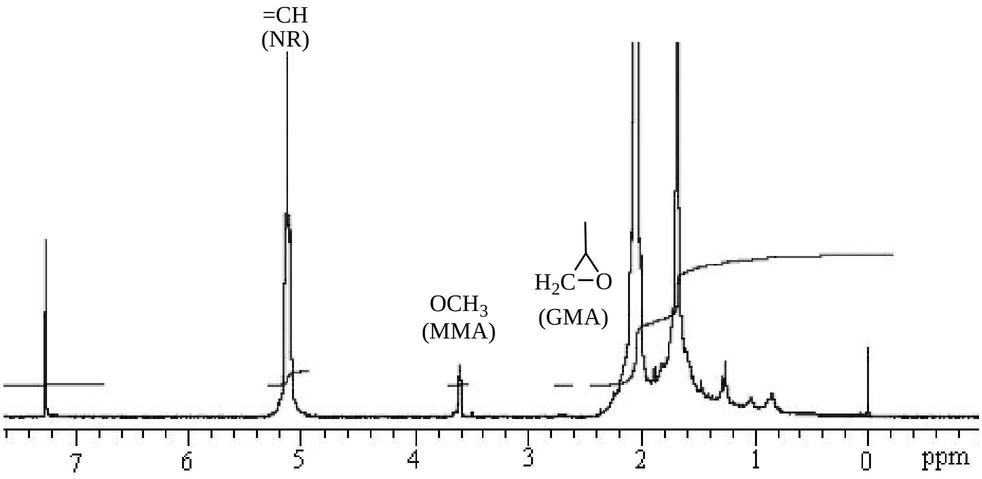


Figure 4.6 ^{1}H-NMR spectrum of 50_2AIBN.

4.2.2.1 Effect of types of initiator on the degree of graftization

To determine the effect of types of initiator on degree of graftization, the monomer mixture of MMA/GMA (90/10 wt/wt%) was fixed at 50 phr based on rubber content. Two types of initiator used were benzoyl peroxide (BPO) and azo-bis-isobutyronitrile (AIBN). The amount of MMA per proton (*MMA*), the amount of isoprene per proton (*NR*), the amount of GMA per proton (*GMA*), the fractions of MMA ($F_{MMA\text{-}g}$) and the fractions of GMA ($F_{GMA\text{-}g}$) in the graft copolymers which were calculated from the different signal areas are given in Table 4.2.

Table 4.2 Graft copolymer compositions of GDNR prepared from different initiators.

GDNR	*NR*	*MMA*	*GMA*	$F_{MMA\text{-}g}$	$F_{GMA\text{-}g}$
50_1BPO	10.310	0.433	0.095	0.820	0.180
50_2BPO	9.820	0.743	0.135	0.847	0.153
50_3BPO	9.530	0.783	0.115	0.872	0.128
50_1AIBN	10.830	0.157	0.060	0.724	0.276
50_2AIBN	9.630	0.283	0.050	0.850	0.150
50_3AIBN	10.330	0.133	0.085	0.611	0.389

As expected, the level of MMA in the graft copolymers was higher than that of GMA because the concentration of GMA used in grafting process was low. The results presented in Table 4.2 also show that, at the same amount of initiator, the BPO initiator led to higher degree of graftization than AIBN initiator. This might be because the half-life time of BPO was longer than that of AIBN. The grafted monomer increased with increasing half-life time ($t_{1/2}$) of the initiator (Kim and Lee, 2003) and the initiator radical of AIBN was more bulky than that of BPO. The schematic diagram showing cleavage of AIBN and BPO initiator are shown in Figure 4.7.

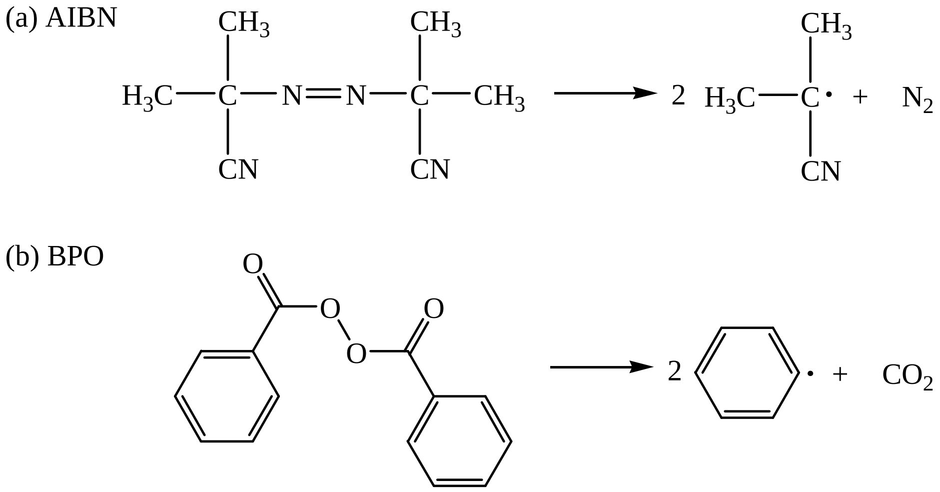


Figure 4.7 Schematic diagram showing cleavage of AIBN (a) and BPO (b).

Although GDNR prepared from BPO initiator showed higher degree of graftization than that prepared from AIBN initiator, it did not dissolve in epoxy resin. This might be because the reactions of reactive sites on the DNR molecules caused gel fraction in graft copolymer (Nakason et al., 2004). Therefore, AIBN was used as an initiator in grafting process in order to study the effect of monomer and initiator concentration on grafting efficiency.

4.2.2.2 Effects of monomer and initiator concentration on the degree of graftization

In this section, the effects of monomer and initiator concentration on degree of graftization of GDNR were investigated. The amounts of monomer mixture were varied from 20 to 75 phr of DNR content. The free radical initiator, azo-bis-isobutyronitrile (AIBN) was used. The amounts of initiator were varied from 1 to 3% based on DNR content.

The amount of MMA per proton (*MMA*), the amount of isoprene per proton (*NR*), the amount of GMA per proton (*GMA*), the fractions of MMA ($F_{MMA\text{-}g}$) and the fractions of GMA ($F_{GMA\text{-}g}$) in the graft copolymers which were calculated from the different signal areas are tabulated in Table 4.3.

Table 4.3 Graft copolymer compositions of GDNR prepared by use of AIBN initiator.

GDNR	**Monomer mixture (phr)**	**AIBN (%)**	***NR***	***MMA***	***GMA***	$F_{MMA\text{-}g}$	$F_{GMA\text{-}g}$
20_1AIBN	20	1	10.470	0.053	0.050	0.516	0.484
20_2AIBN		2	10.390	0.067	0.040	0.625	0.375
20_3AIBN		3	10.490	0.037	0.050	0.423	0.577
30_1AIBN	30	1	10.470	0.083	0.080	0.510	0.490
30_2AIBN		2	10.240	0.150	0.095	0.612	0.388
30_3AIBN		3	9.450	0.093	0.085	0.523	0.477
50_1AIBN	50	1	10.830	0.157	0.060	0.723	0.277
50_2AIBN		2	9.630	0.283	0.050	0.850	0.150
50_3AIBN		3	10.330	0.133	0.085	0.611	0.389
75_1AIBN	75	1	9.950	0.423	0.070	0.858	0.142
75_2AIBN		2	9.400	0.893	0.085	0.913	0.087
75_3AIBN		3	9.830	0.303	0.115	0.725	0.275

The results showed that, for all reaction, the total amount of *MMA* and *GMA* increased until initiator concentration reached 2 phr. When initiator concentration was further increased to 3 phr, the total amount of *MMA* and *GMA* seemed to decrease. This might be because an excess concentration of AIBN initiator generated more homopolymer chain which ultimately resulted in termination of growing chains. The fractions of GMA ($F_{GMA\text{-}g}$) in graft copolymers tended to decrease as the fractions of MMA ($F_{MMA\text{-}g}$) increased.

The results of monomer concentration showed that the total amount of *MMA* and *GMA* increased with an increase of monomer concentration. Generally, the grafted monomer increased with increasing monomer concentration (Jiang and Wilkie, 1998).

Accordingly, it can be concluded that, at 2 phr of AIBN initiator, degree of graftization is in the order of 75_2AIBN>50_2AIBN> 30_2AIBN>20_2AIBN.

Although GDNR prepared using 75 phr monomer mixtures showed the highest grafting efficiency, it was very difficult to precipitate from solution. This could be because more homopolymer occurred.

4.2.3 Characteristics of GDNR prepared for blending with epoxy resin

As presented in section 4.2.2.2, the highest grafting efficiency of GDNR prepared from different monomer concentration was achieved when AIBN initiator concentration was 2 phr. Therefore, in the preparation of GDNR for blending with epoxy resin, the amount of initiator was fixed at 2 phr and the amount of monomer mixture was varied from 20 to 50 phr in order to obtain three different degree of graftization.

4.2.3.1 Molecular weight and molecular structure of DNR and GDNR

Molecular weight of DNR and GDNR were determined before blending with epoxy resin using gel permeation chromatography. The number average molecular weight, M_n, weight average molecular weight, M_w, and molecular weight distribution, MWD, of DNR and GDNR are tabulated in Table 4.4. The results showed that molecular weights of GDNR obtained are lower than that of DNR. This result indicated that the scissions of chain length of DNR occurred in grafting process. The decrease of molecular weight of DNR might be due to the high reaction temperature of grafting process (Kongparakul et al., 2008) and the degradation of natural rubber molecule was found as AIBN initiator was used (Hourston and Romaine, 1991). Moreover, molecular weight of GDNR tended to decrease with increasing monomer mixture concentration. The high reactivity of monomeric radical might enhance chain scission in this system. In general, MWD of DNR and GDNR was only slightly different. However, 30_2AIBN(L) seemed to show the highest MWD.

Table 4.4 Molecular weight and molecular weight distribution of DNR and GDNR.

Types of rubber	**M_n (g/mol)**	**M_w (g/mol)**	**MWD**
DNR	55,984	135,487	2.420
20_2AIBN(L)	46,715	105,691	2.262
30_2AIBN(L)	25,991	70,574	2.715
50_2AIBN(L)	24,684	57,260	2.320

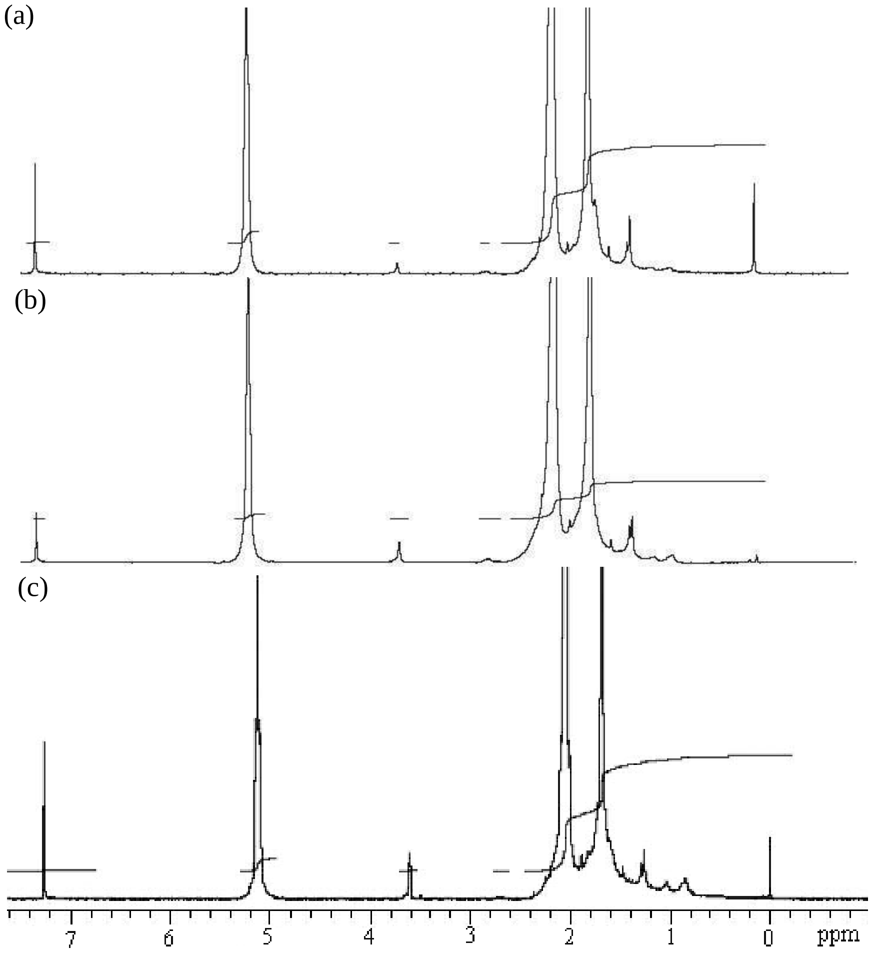


Figure 4.8 ^{1}H-NMR spectra of GDNR; (a) 20_2AIBN(L), (b) 30_2AIBN(L) and (c) 50_2AIBN(L).

Figure 4.8 illustrates ^{1}H-NMR spectra of GDNR which were prepared for blending with epoxy resin. The results showed that the level of monomer attached to DNR increased with increasing monomer concentration.

4.2.3.2 Degree of graftization

Table 4.5 illustrates graft copolymer compositions of GDNR which were used in the blends. The results showed that degree of graftization of GDNR increased with an increase of monomer concentration. Hence, the degree of graftization is in the order of 50_2AIBN(L)>30_2AIBN(L)>20_2AIBN(L). These results were in agreement with the results described in section 4.2.2.2.

Table 4.5 Graft copolymer compositions of GDNR prepared for blending with epoxy resin.

GDNR	***NR***	***MMA***	***GMA***	$F_{MMA\text{-}g}$	$F_{GMA\text{-}g}$
20_2AIBN(L)	10.290	0.052	0.038	0.579	0.421
30_2AIBN(L)	10.050	0.117	0.073	0.617	0.383
50_2AIBN(L)	10.230	0.220	0.055	0.800	0.200

4.3 Mechanical and morphological properties of depolymerized natural rubber (DNR)/epoxy resin blends

4.3.1 Mechanical properties of DNR/epoxy resin blends

In this section, depolymerized natural rubber (DNR), in an amount of 0.5, 1, 2 and 3 phr, were blended with epoxy resin and cured with polyamide at room temperature for 4 h. The mechanical properties of DNR/epoxy resin blends are summarized in Table 4.6.

4.3.1.1 Impact properties of DNR/epoxy resin blends

The results of impact strength were reported in terms of energy absorbed per unit of cross sectional area under the notch. The impact strength of neat epoxy and DNR/epoxy resin blends are graphically compared in Figure 4.9. The results showed that, with an exception of the blend containing 3 phr of DNR, the impact strength of epoxy resin was generally improved when DNR was added.

Table 4.6 Mechanical properties of DNR/epoxy resin blends.

Designation	Amounts of DNR (phr)	Impact strength (kJ/m^2)	Flexural modulus (GPa)	Flexural strength (MPa)	Flexural strain (%)
Neat epoxy	0	2.292±0.224	2.504±0.106	99.488±2.440	7.771±0.582
0.5_DNR	0.5	2.344±0.259	2.376±0.037	96.299±4.012	7.957±0.818
1_DNR	1.0	2.544±0.179	2.368±0.065	96.008±4.125	8.482±0.768
2_DNR	2.0	2.303±0.159	2.309±0.077	94.623±2.466	7.673±0.450
3_DNR	3.0	1.380±0.104	2.275±0.084	92.640±3.619	6.827±0.621

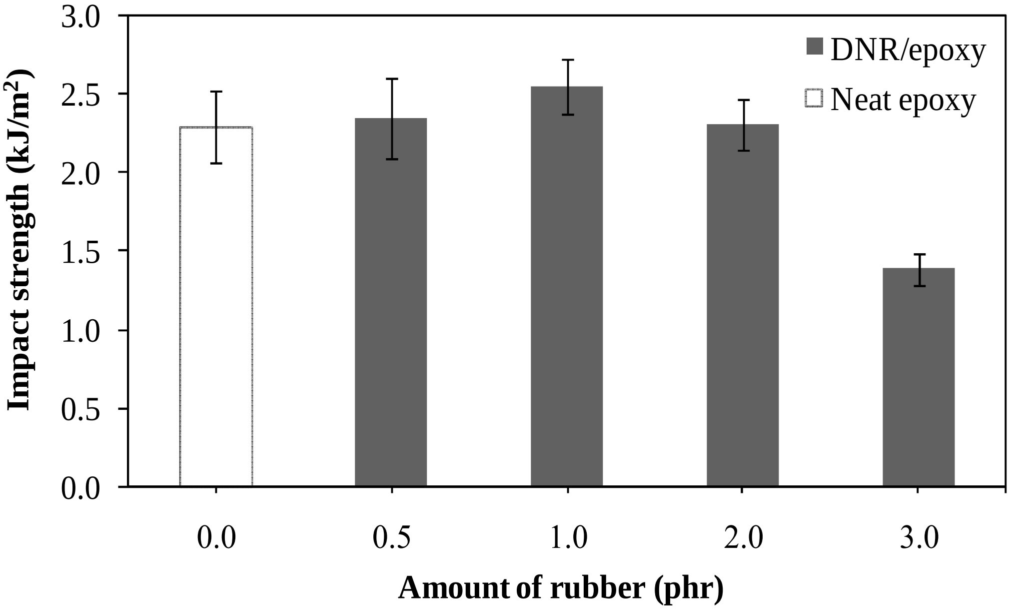


Figure 4.9 Impact strength of neat epoxy and DNR/epoxy resin blends.

For the blends containing 0.5, 1 and 2 phr of rubber, the impact strength of the blends was higher than that of the neat epoxy. This might be because DNR which presented as rubbery particles in matrix acted as stress concentrator creating shear yielding and/or crazing in the matrix.

In addition, some of rubber molecules might dissolve in epoxy matrix leading to flexibility of epoxy resin. The blend containing 1 phr of rubber showed the highest impact strength among the DNR/epoxy resin blends. This might be because both toughening and flexibility effects could be operative, resulting in maximum improvement in impact strength (Kumar and Kothandaraman, 2008). However, the impact strength of the blend containing 3 phr of rubber was lower than that of neat epoxy. This could be due to rubber aggregation. The large size of rubbery particles might lead to poor adhesion between the particle and matrix. This agreed with morphology of the blends (see section 4.3.2).

4.3.1.2 Flexural properties of DNR/epoxy resin blends

The results of flexural strain at break (%) of epoxy resin were improved when DNR was added as seen in Figure 4.10 and Figure 4.11

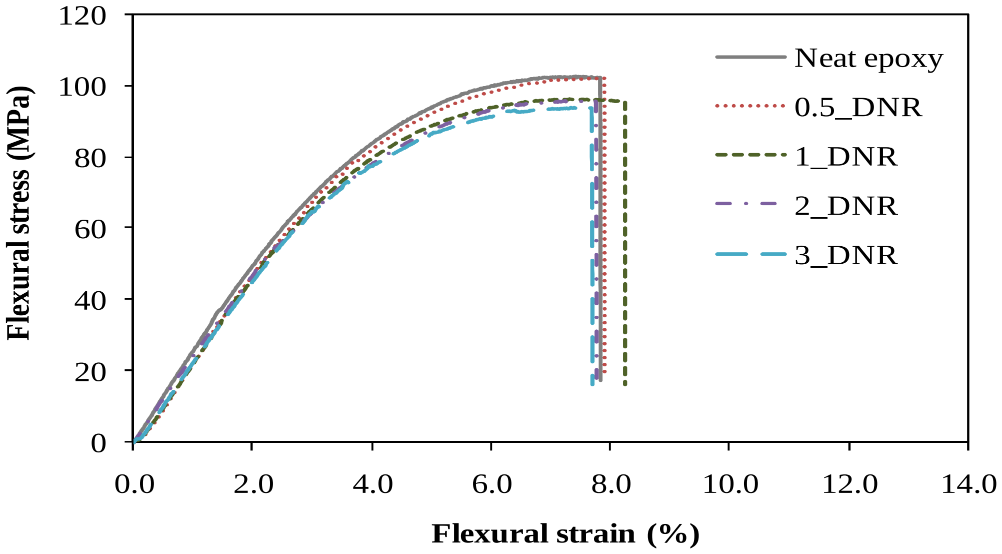


Figure 4.10 Flexural curves of neat epoxy and DNR/epoxy resin blends.

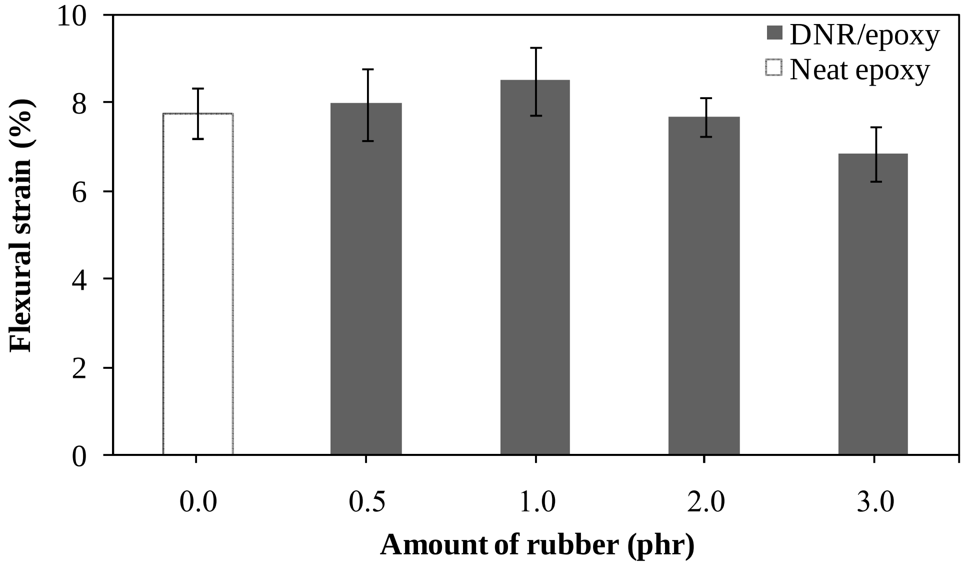


Figure 4.11 Flexural strain (%) of neat epoxy and DNR/epoxy resin blends.

The flexural strain of the blends was in agreement with the results of impact strength. The blend containing 1 phr of rubber showed the highest flexural strain. This could be seen in Figure 4.10. This shows that the rubber modified epoxy has undergone higher percent of strain before failure, which was significantly contributed in enhancing the toughness property of the epoxy resin (Kumar and Kothandaraman, 2008). Nevertheless, in agreement with many studies (Chikhi et al., 2002; Saadati et al., 2005; Chuayjuljit et al., 2006), the addition of rubber into epoxy resin slightly brought down flexural strength and flexural modulus. The reduction in flexural strength and flexural modulus are graphically shown in Figure 4.12 and Figure 4.13, respectively. This was not unusual because soft segment structure of DNR had low modulus (Chuayjuljit et al., 2006 and Kumar and Kothandaraman, 2008).

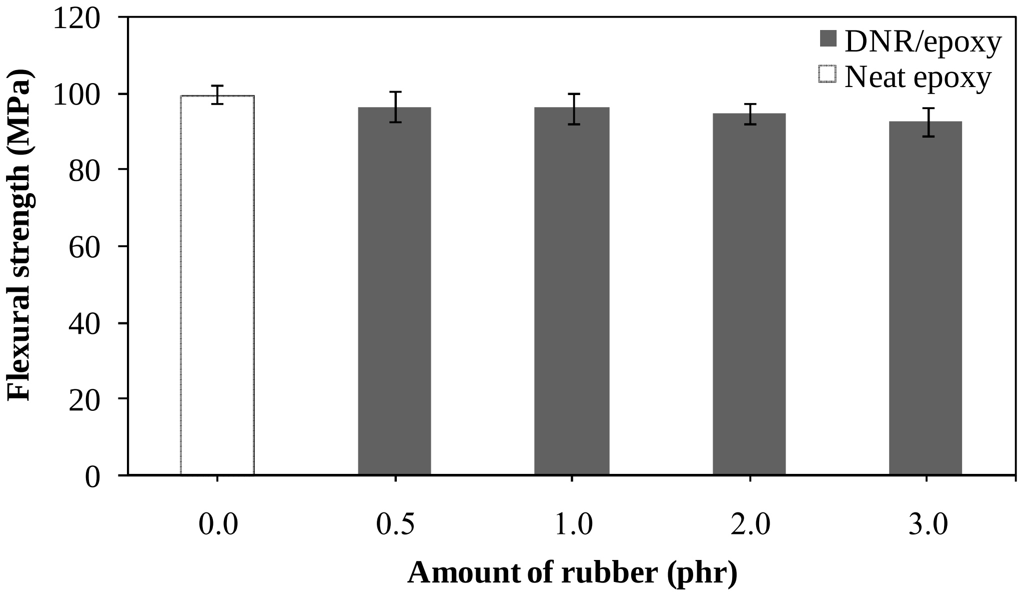


Figure 4.12 Flexural strength of neat epoxy and DNR/epoxy resin blends.

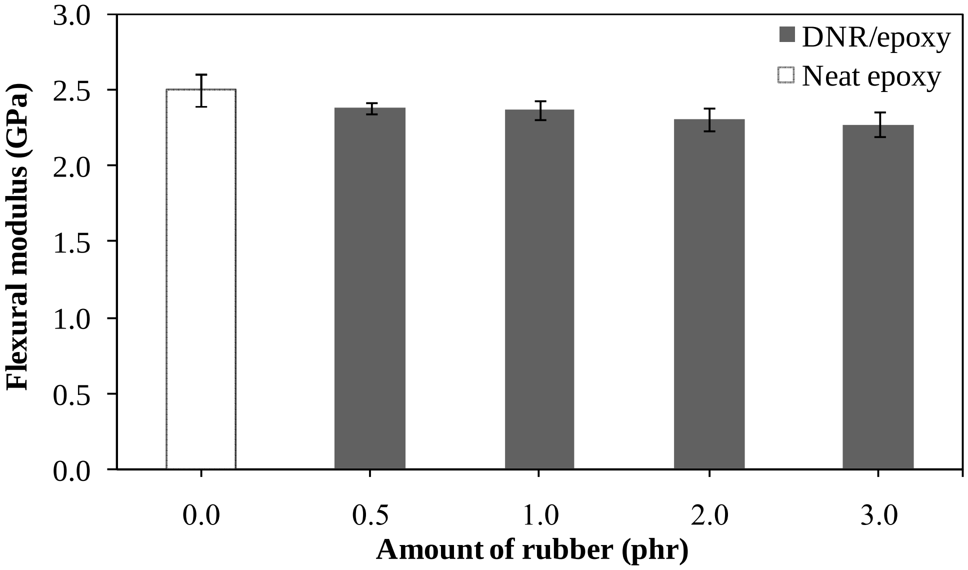
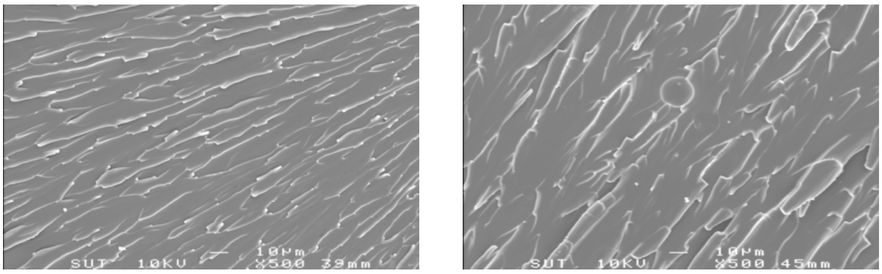


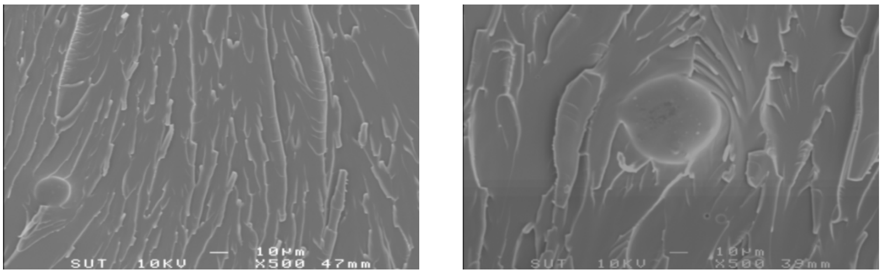
Figure 4.13 Flexural modulus of neat epoxy and DNR/epoxy resin blends.

4.3.2 Morphological properties of DNR/epoxy resin blends

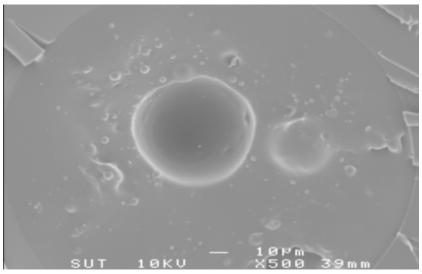
In order to correlate the mechanical properties of modified epoxy resin with the morphology, particularly, searching for a correlation between particle size of the rubber phase and impact strength results, the fracture surfaces of neat epoxy and DNR/epoxy blends were analyzed by scanning electron microscope (SEM). SEM micrographs are shown in Figure 4.14. Inspection of Figure 4.14 (a) shows ridged surface with cracks in different planes for unmodified epoxy. SEM micrographs of rubber modified epoxy resin, Figure 4.14 (b)-(e), reveal two phases structure which comprised of the discrete rubber particles and the epoxy matrix.



(a) Neat epoxy (b) 0.5_DNR



(c) 1_DNR (d) 2_DNR



(e) 3_DNR

Figure 4.14 SEM micrographs at 500x magnification of epoxy and DNR/epoxy resin blends.

The average particle sizes of DNR in epoxy matrix for each blend are shown in Table 4.7. It was found that the average particle size of DNR increased with increasing rubber content. This implied that rubber tended to coalesce as rubber content was increased. This was due to low compatibility between DNR and epoxy matrix (Saadati et al., 2005). When particle size was too large, the interaction between the particle and the matrix was not satisfactory (Ramos et al., 2005). Furthermore, the blend containing 3 phr of rubber showed the very smooth glassy fractured surface.

This indicated a brittle fracture which accounts for its poor impact strength (Ratna, 2001). In Table 4.7, it could be seen that the particle size of dispersed rubbery domains of 0.5_DNR was closed to that of 1_DNR. However, the blend containing 0.5 phr of DNR or 0.5_DNR showed lower impact strength than the blend containing 1 phr of DNR. This might be due to higher volume fraction of rubber in 1_DNR. Higher volume fraction of rubber led to higher improvement in toughness of epoxy resin (Thomas et al., 2008). Similar results had been reported by Kumar and Kothandaraman (2008).

Table 4.7 DNR particle size in epoxy resins modified by different amount of DNR.

Designation	**Rubber content (phr)**	**Particle size of DNR (μm)**
0.5_DNR	0.5	14.09±5.38
1_DNR	1.0	16.48±6.23
2_DNR	2.0	54.93±21.55
3_DNR	3.0	70.29±24.46

From mechanical and morphological properties of DNR/epoxy resin blends, it can be concluded that the blend containing 1 phr of DNR showed the best toughness improvement. Therefore, this optimum condition was chosen to study effect of degree of graftization on the mechanical and morphological properties of GDNR/epoxy resin blends.

4.4 Mechanical and morphological properties of grafted DNR (GDNR)/epoxy resin blends

In this section, three GDNRs, which were 20_2AIBN(L), 30_2AIBN(L) and 50_2AIBN(L), were used to study the effect of degree of graftization on the mechanical and morphological properties of GDNR/epoxy resin blends. As reported in Table 4.5 (see section 4.2), the degree of graftization of GDNR is in the order of 50_2AIBN(L)>30_2AIBN(L)>20_2AIBN(L). The amount of GDNR in the blends was 1 phr, since this composition showed the highest toughness as mentioned in section 4.3.

4.4.1 Mechanical properties of (G)DNR/epoxy resin blends

The mechanical properties of (G)DNR/epoxy resin blends are summarized in Table 4.8.

4.4.1.1 Impact properties of (G)DNR/epoxy resin blends

The impact strength of neat epoxy and (G)DNR/epoxy resin blends are graphically compared in Figure 4.15. It was found that the incorporation of DNR and GDNR into epoxy resin improved impact strength of epoxy resin. In addition, it can be seen that the impact strength of GDNR/epoxy blends was higher than that of DNR/epoxy blends. This was expected because GDNRs were more polarity than DNR. Moreover, there were some epoxide groups in grafted GMA. These could increase interfacial adhesion between rubbery particles and epoxy matrix. The impact strength of 1_DNR, 1_20_2AIBN(L), 1_30_2AIBN(L) and 1_50_2AIBN(L) was 2.544, 3.064, 3.703 and 2.888 kJ/m^2, respectively. Compared to neat epoxy, the impact strength of those blends increased 10%, 34%, 63% and 26%, respectively. It could be seen that, with an exception of 1_50_2AIBN(L), the impact strength increased with increasing degree of graftization. This might be because an increase of acrylic group of the MMA and the epoxy group of GMA onto DNR backbone improved both the compatibility and interfacial adhesion between rubber and epoxy matrix and led to good stress transfer from epoxy matrix. The blend containing 1 phr of 30_2AIBN(L) or 1_30_2AIBN(L) showed the highest impact strength. A possible reason is related to the balance between molecular weight and degree of graftization of GDNR (see section 4.2.3). The impact strength of the blend containing 1 phr of 50_2AIBN(L) was lower than that of 1_30_2AIBN(L) although 50_2AIBN(L) had higher degree of graftization. This might be because of the rigid characteristics of MMA that attached to DNR backbone. Increasing amount of MMA led to more rigid structure of GDNR. Hence, it might not properly act as soft rubbery. Moreover, the molecular weight of rubber had affect toughness of epoxy resin. Molecular weight of 50_2AIBN(L) is the lowest among GDNRs. The GDNR with low molecular weight might not efficiently toughen epoxy resin. Thongpin et al. (2006) suggested that the higher the molecular weight of epoxidized natural rubber (ENR) gave the better mechanical properties improvement of epoxy resin. Another reason might be because 30_2AIBN(L) gave higher rubber particle size distribution than 50_2AIBN(L) (see Table 4.9). Pearson and Yee (1991) suggested that a higher rubber particle size distribution should result in a greater increase in fracture toughness in rubber-modified epoxies.

Table 4.8 Mechanical properties of (G)DNR/epoxy resin blends (rubber content = 1 phr).

Designation	**Impact strength (kJ/m^2)**	**Flexural modulus (GPa)**	**Flexural strength (MPa)**	**Flexural strain (%)**
Neat epoxy	2.292±0.224	2.504±0.106	99.488±2.440	7.771±0.582
1_DNR	2.544±0.179	2.368±0.065	96.008±4.125	8.482±0.768
1_20_2AIBN(L)	3.064±0.343	2.359±0.157	95.379±2.281	8.734±0.345
1_30_2AIBN(L)	3.703±0.297	2.387±0.054	95.268±3.501	9.415±0.622
1_50_2AIBN(L)	2.888±0.457	2.362±0.101	95.712±3.847	8.014±0.363

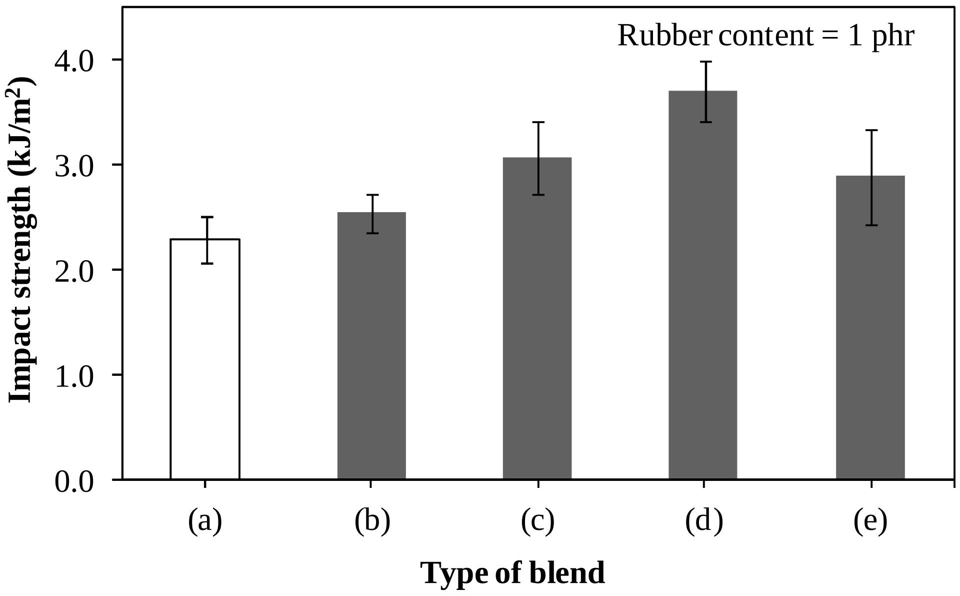


Figure 4.15 Impact strength of neat epoxy and (G)DNR/epoxy resin blends; (a) Neat epoxy, (b) 1_DNR, (c) 1_20_2AIBN(L), (d) 1_30_2AIBN(L) and (e) 1_50_2AIBN(L).

4.4.1.2 Flexural properties of (G)DNR/epoxy resin blends

Flexural strain at break (%) of epoxy resin was improved when GDNR was added as shown in Figure 4.16 and Figure 4.17. Generally, with an exception for 1_50_2AIBN(L), flexural strain of the blends containing 1 phr of GDNR increased with increasing degree of graftization. The blend containing 1 phr of 30_2AIBN(L) showed the highest flexural strain. This illustrated that the degree of graftization had affected toughness of rubber modified epoxy. It implied that compatibility between rubber and epoxy matrix was enhanced and led to an improvement of toughness of epoxy matrix. However, in case of 1_50_2AIBN(L), flexural strain at break was out of trend. It might be explained in the same way as impact strength results.

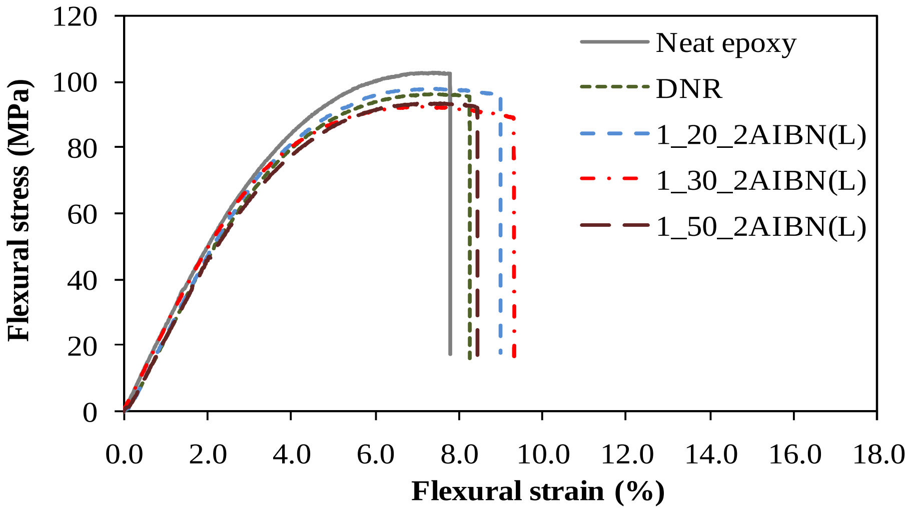


Figure 4.16 Flexural curves of neat epoxy and (G)DNR/epoxy resin blends.

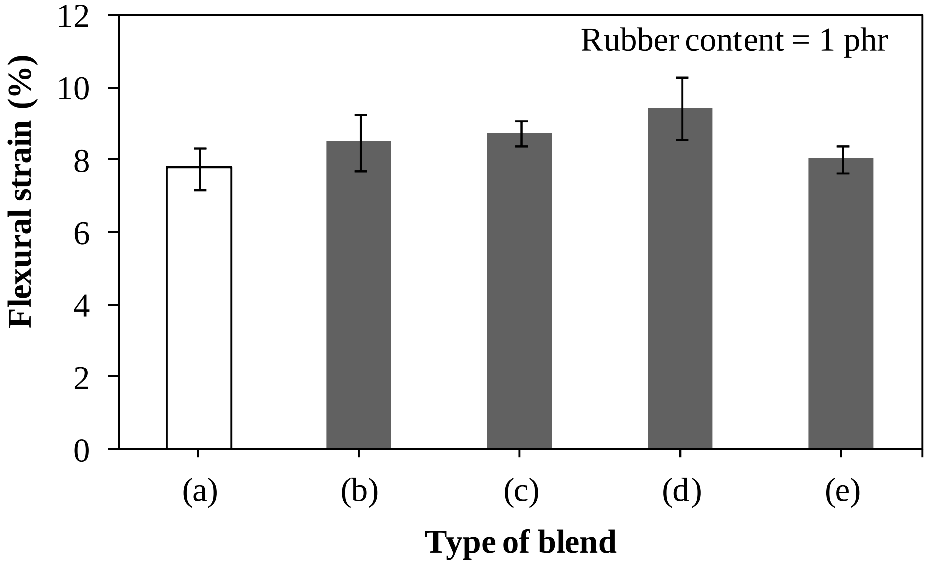


Figure 4.17 Flexural strain of neat epoxy and (G)DNR/epoxy resin blends; (a) Neat epoxy, (b) 1_DNR, (c) 1_20_2AIBN(L), (d) 1_30_2AIBN(L) and (e) 1_50_2AIBN(L).

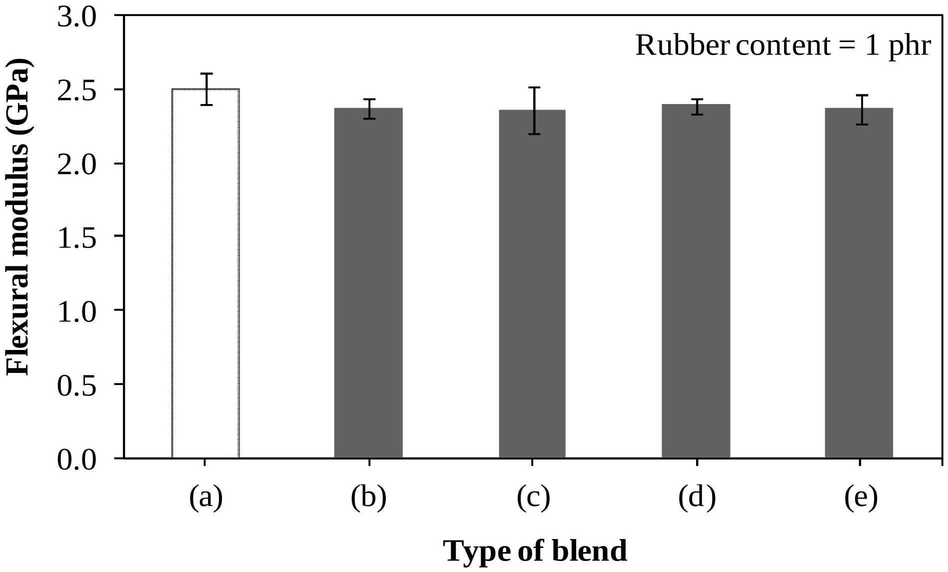


Figure 4.18 Flexural modulus of neat epoxy and (G)DNR/epoxy blends; (a) Neat epoxy, (b) 1_DNR, (c) 1_20_2AIBN(L), (d) 1_30_2AIBN(L) and (e) 1_50_2AIBN(L).

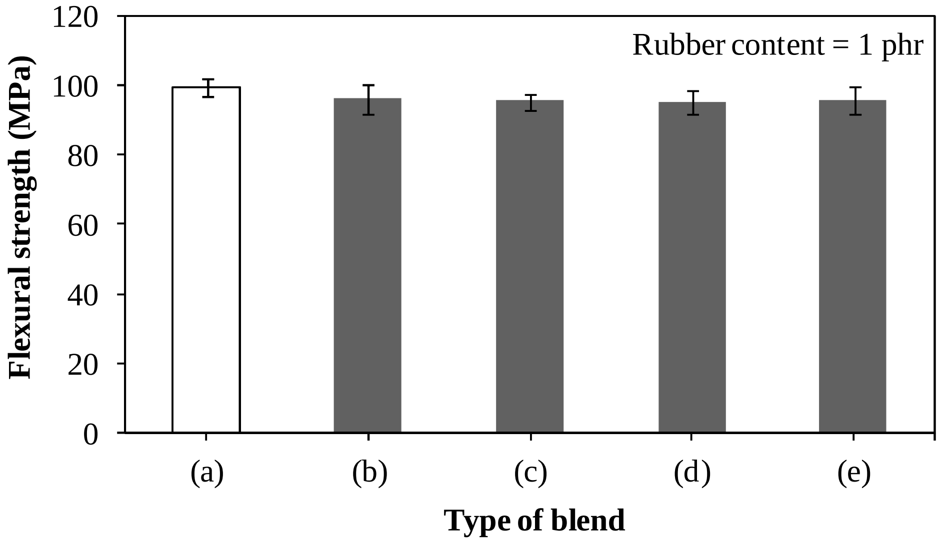


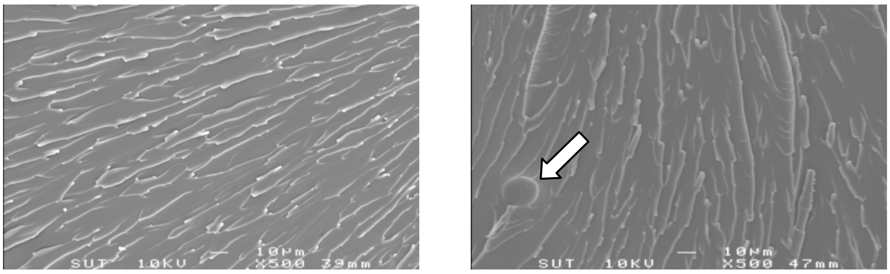
Figure 4.19 Flexural strength of neat epoxy and (G)DNR/epoxy resin blends; (a) Neat epoxy, (b) 1_DNR, (c) 1_20_2AIBN(L), (d) 1_30_2AIBN(L) and (e) 1_50_2AIBN(L).

In contrast to flexural strain, flexural modulus and flexural strength slightly decreased when GDNR was incorporated into epoxy resin as shown in Figure 4.18 and Figure 4.19, respectively. This is not unusual because soft segment structure of GDNR has low modulus (Chuayjuljit et al., 2006 and Kumar and Kothandaraman, 2008).

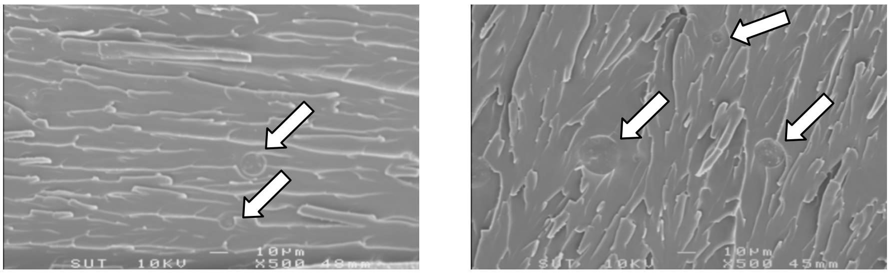
4.4.2 Morphological properties of (G)DNR/epoxy resin blends

SEM micrographs of (G)DNR/epoxy resin blends are shown in Figure 4.20 (a)-(e). The average particle sizes of GDNR are shown in Table 4.9. It could be seen that particle sizes of GDNR were smaller than those of DNR. The particle sizes of GDNR generally decreased with increasing degree of graftization. This might be because the compatibility between rubber and matrix was enhanced by grafted monomer on GDNR chain.

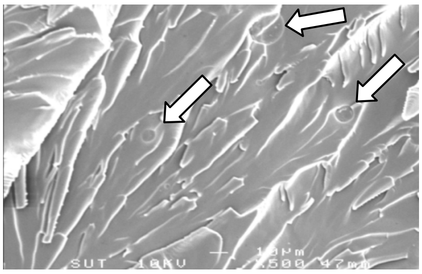
It also implied that the interfacial adhesion between GDNR rubber and epoxy matrix was improved. Therefore, the fracture toughness of the blends was enhanced. Moreover, in case of 1_30_2AIBN(L), the rubber particle showed several sizes and caused higher enhancement of toughness. A higher rubber particle size distribution showed a greater increase in fracture toughness (Pearson and Yee, 1991). Therefore, the toughness of 1_30_2AIBN(L) was higher than that of 1_50_2AIBN(L). This might be due to combination of rubber particle size distribution effect and compatibility between rubber and epoxy matrix.



(a) Neat epoxy (b) 1_DNR(L)



(c) 1_20_2AIBN(L) (d) 1_30_2AIBN(L)



(e) 1_50_2AIBN(L)

Figure 4.20 SEM micrographs at 500x magnification of epoxy and (G)DNR/epoxy resin blends. The rubber particles are indicated by arrows.

Table 4.9 (G)DNR particle size in the blends prepared from different (G)DNR type.

Designation	**Particle size of (G)DNR (µm)**
1_DNR	16.48±6.23
1_20_2AIBN(L)	13.41±4.15
1_30_2AIBN(L)	11.15±8.82
1_50_2AIBN(L)	11.84±4.92

4.5 Mechanical and morphological properties of short fiber glas reinforced (G)DNR modified epoxy resin

Studies of modified natural rubber/epoxy resin blends in the present work intend to develop tough epoxy matrix for applying in composite production. As stated in previous section, 30_2AIBN(L)/epoxy resin blend or 1_30_2AIBN(L) showed the highest toughness. Therefore, the effect of this blend on properties of short fiber glass/epoxy composites was evaluated. Three different short fiber glass reinforced epoxy composites which included fiber glass/pure epoxy composite, DNR/fiber glass/epoxy composite and 30_2AIBN(L)/fiber glass/epoxy composite were prepared. The amount of fiber glass (GF) in the composites was 5 wt%. The three different composites were represented by 5% GF, 1_DNR_5% GF and 1_30_2AIBN(L)_5% GF, respectively.

4.5.1 Mechanical properties of (G)DNR/fiber glass/epoxy composites

Impact strength and flexural modulus of epoxy resin were improved when the 5 wt% of fiber glass was added but flexural strength and flexural strain were decreased. The reduction of flexural strength and flexural strain when the fiber glass was added might be due to voids in the composites and poor wettability between fiber and matrix. Moreover, this decrease could be related to the uneven and random fiber orientation, relatively low volume percentage, and short lengths of the fiber (Kaynak, Arikan, and Tincer, 2003). With incorporation of 1 phr of DNR, the impact strength and flexural strain of 1_DNR_5% GF were higher than that of composite made of 5 wt%_GF which presented an increase of 9.4%. This implied that the addition of DNR could improve toughness of GF/epoxy composites.

Furthermore, the toughness of 1_30_2AIBN(L)_5% GF was higher than that of 1_DNR_5% GF (about 23%). This might be because functional group of MMA and GMA that attached to DNR could enhance compatibility between rubber and epoxy matrix. However, flexural modulus of both composites was slightly decreased when rubbers were added. Nevertheless, it was still higher than that of pure epoxy resin. The mechanical properties are summarized in Table 4.10 and graphically compared in Figures 4.21-4.25.

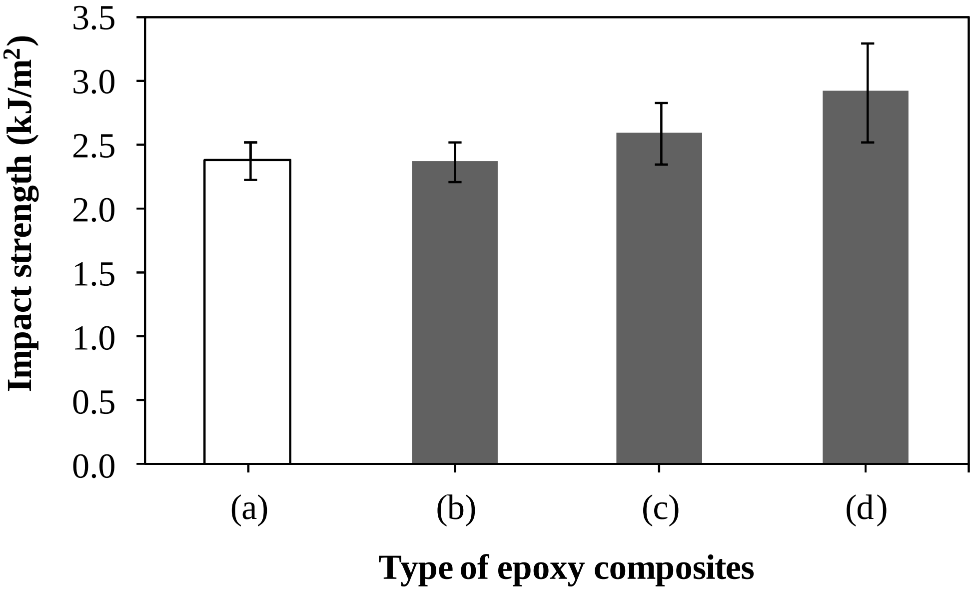


Figure 4.21 Impact strength of neat epoxy and epoxy composites; (a) Neat epoxy, (b) 5% GF, (c) 1_DNR_5%GF and (d) 1_30_2AIBN(L)_5% GF.

Table 4.10 Mechanical properties of neat epoxy, 5 wt% fiber glass/epoxy composites and 5 wt% fiber glass/(G)DNR/epoxy composites.

Designation	**Impact strength (kJ/m^2)**	**Flexural modulus (GPa)**	**Flexural Strength (MPa)**	**Flexural strain (%)**
Neat epoxy	2.292±0.224	2.504±0.106	99.488±2.440	7.771±0.582
5% GF	2.367±0.150	2.701±0.132	60.262±4.202	2.441±0.196
1_DNR_5% GF	2.590±0.240	2.627±0.126	59.301±4.002	2.463±0.328
1_30_2AIBN(L)_5% GF	2.917±0.384	2.670±0.062	59.942±3.291	2.692±0.199

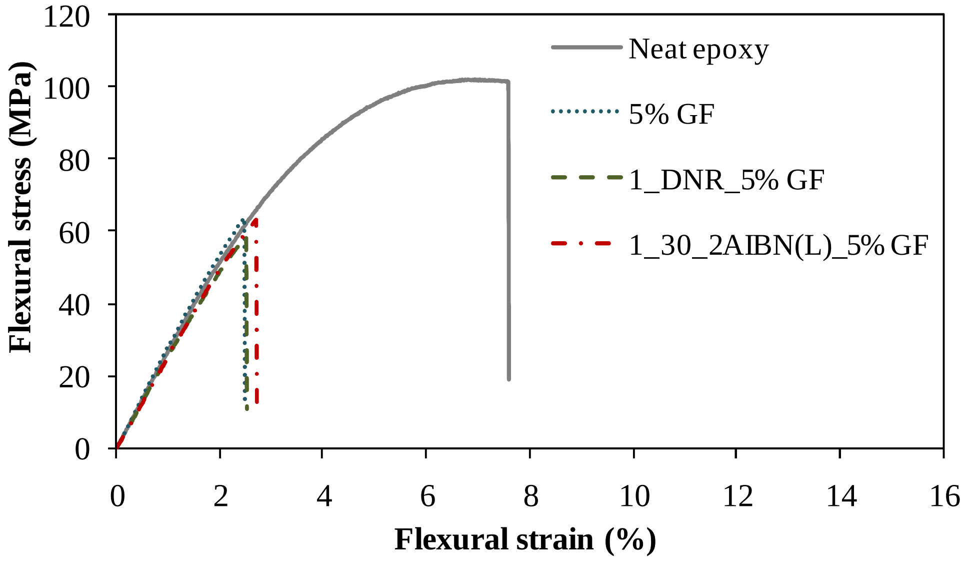


Figure 4.22 Flexural curves of neat epoxy, 5 wt% fiber glass/epoxy composites and 5 wt% fiber glass/(G)DNR/epoxy composites.

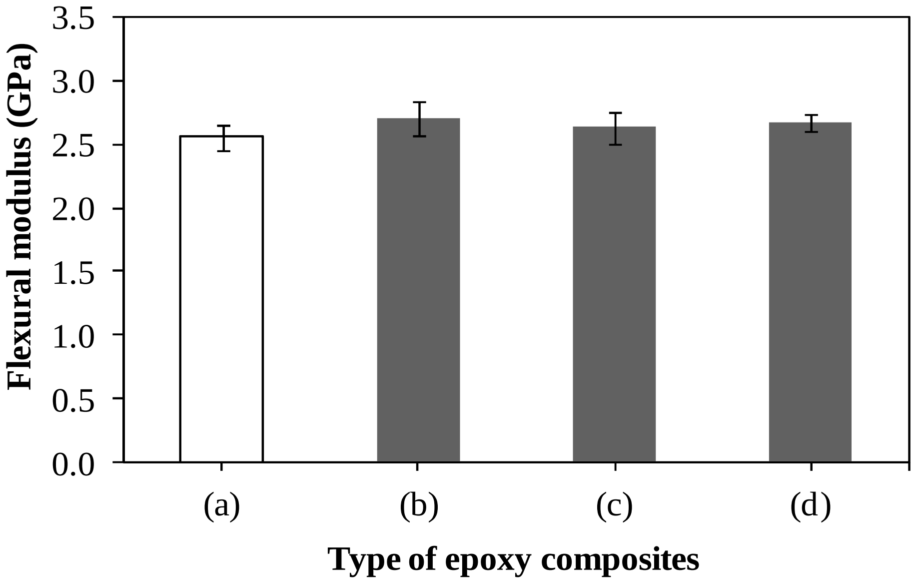


Figure 4.23 Flexural modulus of neat epoxy and epoxy composite; (a) Neat epoxy, (b) 5% GF, (c) 1_DNR_5% GF and (d) 1_30_2AIBN(L)_5% GF.

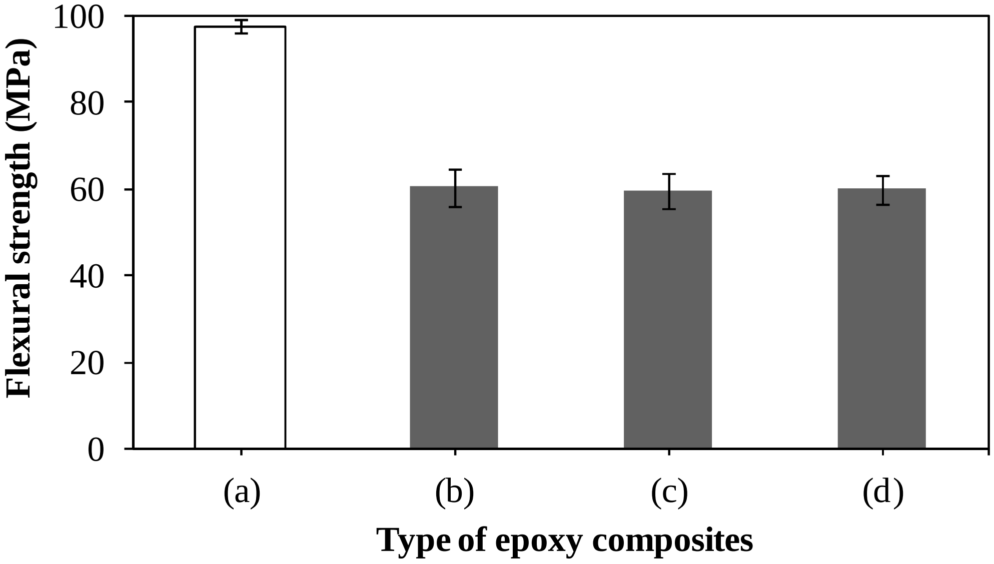


Figure 4.24 Flexural strength of neat epoxy and epoxy composite; (a) Neat epoxy, (b) 5% GF, (c) 1_DNR_5% GF and (d) 1_30_2AIBN(L)_5% GF.

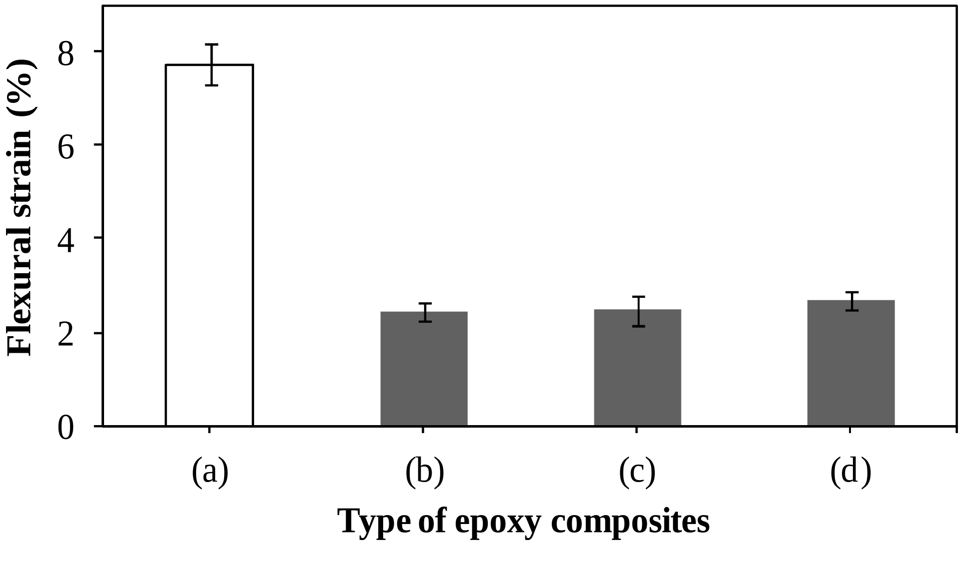
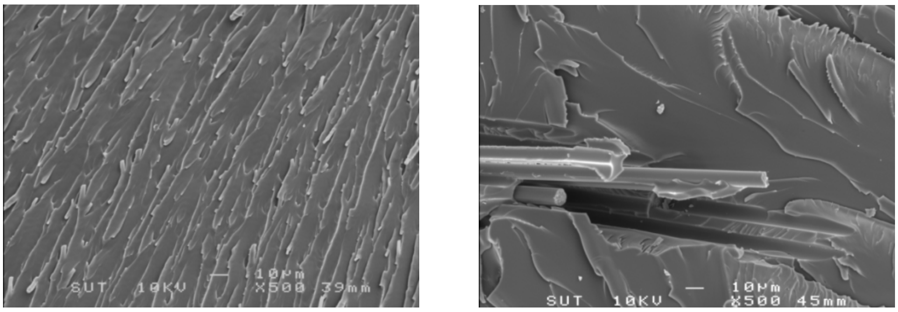


Figure 4.25 Flexural strain (%) of neat epoxy and epoxy composite; (a) Neat epoxy, (b) 5% GF, (c) 1_DNR_5% GF and (d) 1_30_2AIBN(L)_5% GF.

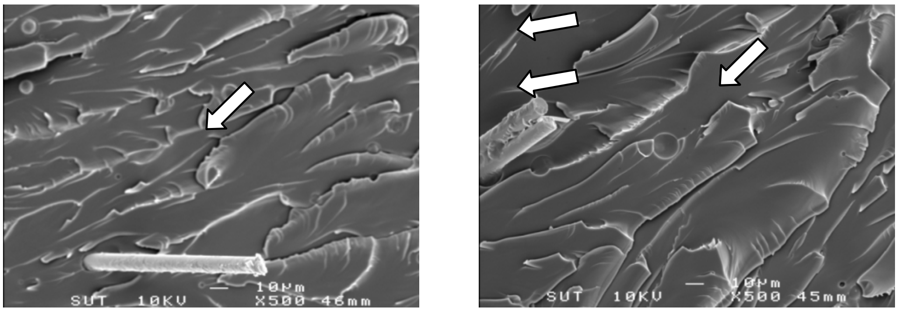
From the impact results obtained, it can be concluded that modified natural rubber/epoxy resin blends, particularly 1_30_2AIBN(L) which showed the highest toughness (see section 4.4), can be used as toughening material for epoxy composites.

4.5.2 Morphological properties of (G)DNR/fiber glass/epoxy composites

Fracture surfaces of fiber glass/epoxy composites are shown in Figure 4.26.



(a) Neat epoxy (b) 5% GF



(c) 1_DNR_5% GF (d) 1_30_2AIBN(L)_5% GF

Figure 4.26 SEM micrographs at 500x magnification of epoxy and epoxy composites. The rubber particles are indicated by arrows.

The fiber glass surface of 5% GF epoxy composites shown in Figure 4.26 (b) presented the clean surface of pulled out fiber. It indicated that the surface adhesion between fiber and epoxy matrix was not good. This might cause the reduction in flexural strength and strain. SEM micrographs of 1_DNR_5% GF and 1_30_2AIBN(L)_5% GF show the rubber particle sizes about 15 and 8 µm, respectively. The decrease in size of rubbery particle implied better compatibility between 30_2AIBN(L) and epoxy resin. This supports the improvement of impact strength of 1_30_2AIBN(L)_5% GF.

CHAPTER V

CONCLUSIONS AND SUGGESTIONS FOR FURTHER WORK

5.1 Conclusions

Depolymerized natural rubber (DNR) was prepared following Tanaka et al., (1999). The molecular weight and molecular weight distribution of DNR were 55,984 g/mol and 2.420, respectively. The effects of monomer concentration, initiator concentration and types of initiator on the degree of graftization of depolymerized natural rubber (DNR) grafted with MMA/GMA (GDNR) were studied. The BPO initiator led to higher degree of graftization than AIBN initiator. However, GDNRs prepared using BPO as an initiator did not completely dissolve in epoxy resin. Therefore, AIBN was used as an initiator in grafting process in order to study the effects of monomer and initiator concentration on degree of graftization. The total amount of *MMA* and *GMA* increased until initiator concentration reached 2 phr. When initiator concentration was further increased to 3 phr, the total amount of *MMA* and *GMA* seemed to decrease. The fraction of *GMA* in graft copolymers tended to decrease as the fractions of *MMA* increased. The results of monomer concentration showed that the total amount of *MMA* and *GMA* increased with an increase of monomer concentration. The molecular weight of GDNR tended to decrease with increasing monomer mixture concentration.

The effects of DNR content on morphological and mechanical properties of DNR/epoxy resin blends were evaluated. The blend containing 1 phr of DNR showed the highest impact strength and flexural strain. The reduction in flexural strength and flexural modulus were happened. SEM micrographs of DNR modified epoxy resin revealed two phases structure which comprised of the discrete rubber particles and the epoxy matrix. The average particle size of DNR increased with increasing rubber content.

The effects of degree of graftization of GDNR on morphological and mechanical properties of GDNR/epoxy resin blends were determined. The graft copolymer led to an improvement of toughness of epoxy matrix. The 1_30_2AIBN showed the highest toughness. With an exception of 1_50_2AIBN, the impact strength and flexural strain increased with increasing degree of graftization. Flexural modulus and flexural strength decreased when GDNR was incorporated into epoxy resin. The average particle sizes of GDNR generally decreased with increasing degree of graftization.

The studies of short fiber glass reinforced (G)DNR modified epoxy resin were also performed. The impact strength and flexural strain of 1_30_2AIBN(L)_5% GF was higher than that of 1_DNR_5% GF. Moreover, the impact strength and flexural modulus of 1_30_2AIBN(L)_5% GF were higher than that of neat epoxy.

5.2 Suggestions for further work

The main interesting topics for the further study related to this research should be as follows:

(i) an investigation of the effect of other types of monomer and initiator on the degree of graftization of GDNR

(ii) an evaluation of the effect of other types of GDNR on the properties of GDNR/epoxy resin blends and

(iii) a study of the effect of other types of fiber on the properties of GDNR/epoxy composites.

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APPENDIX A

PUBLICATION

STUDIES OF NATURAL RUBBER-MODIFIED EPOXY RESIN

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Abstract: Epoxy resin is one of the most important thermosetting polymers due to its interesting properties such as high tensile strength and modulus, excellent chemical resistance and good dimension stability. Nevertheless, in some particular applications of epoxy resins, e.g. structural and automotive applications, high impact strength is required. One of the most successful methods to improve impact strength of epoxy resin is blending with synthetic reactive liquid elastomers [1]. However, there are attempts to use natural rubber because it is abundant and comes from renewable resource [2-3]. The aim of this research was to improve impact strength of diglycidyl ether of bisphenol A type epoxy resin by blending with depolymerized natural rubber grafted with methyl methacrylate/glycidyl methacrylate (GDNR). Depolymerized natural rubber (DNR) was prepared by adding a carbonyl compound to natural rubber latex solution and subjecting the mixture to air oxidation in the presence of a radical forming agent at 70 °C [4]. Monomer mixtures of methyl methacrylate and glycidyl methacrylate were grafted onto DNR backbone. The synthesized graft copolymer was characterized by proton nuclear magnetic resonance (^{1}H-NMR) analysis. The amounts of GDNR in the blends were 1, 2, and 3 parts per hundred of epoxy resin (phr). Tensile and impact tests were performed to observe mechanical behaviour of the neat epoxy resin and the blends.

Introduction

Epoxy resins in the cured state have many desirable properties such as high modulus and tensile strength, excellent chemical and solvent resistance. However, it is extremely brittle. Hence, toughening of epoxy resin has been the subject of intense investigation throughout the world. One of the most successful methods to improve impact strength of epoxy resin is blending with synthetic reactive liquid elastomers [1]. In order to achieve this outcome, the rubber must initially dissolved and become dispersed on a molecular level in the epoxy, but be encouraged to precipitated out when epoxy crosslinking occurs.

Nowadays, there are attempts to use natural rubber because it is abundant and comes from renewable resource. Several studies have been done on toughening epoxy resin using natural rubber [2-3]. As previously discussed, rubber need to be initially dissolved in epoxy resin. This can be done by increasing polarity of natural rubber or reducing molecular weight of rubber. Molecular weight of natural rubber can be reduced either by ozonolysis, photolysis or chemical depolymerization [4].

In addition, in order to achieve an efficient stress transfer between the rubber and the matrix, rubber must have functional groups which can form chemical bonds with epoxy matrix or can promote interfacial adhesion between rubber particle and matrix. Natural rubber can be functionalized either by epoxidation or grafting with various monomers. Monomers including methyl methacrylate, and maleic anhydride are the most frequently studied [5-6].

In this work, depolymerized natural rubber was prepared and grafted with methyl methacrylate and glycidyl methacrylate. Grafted depolymerized natural rubber was used as a toughening agent for epoxy resin.

Materials and Methods

Materials: A high ammonia-concentrated natural rubber latex containing 62% dried rubber was supplied by Thai Hua, Ltd., Udontani, Thailand. Deionized water, methyl ethyl ketone (MEK, Carlo Erba), potassium persulfate ($K_2S_2O_8$, Aldrich), potassium hydroxide (KOH, Aldrich) were used in the preparations of depolymerized natural rubber (DNR). Calcium chloride ($CaCl_2$, Carlo Erba) was used to coagulate DNR. The n-hexane (Carlo Erba) was used to dissolve DNR. Methyl alcohol (Carlo Erba) was used to re-precipitate DNR. Toluene (Carlo Erba) was used as a solvent in the grafting DNR. Methyl methacrylate (MMA, Aldrich) and glycidyl methacrylate (GMA, Aldrich) were used as grafted monomers onto DNR backbone. Initiator for grafting process was azo-bis-isobutyronitrile (AIBN, Carlo Erba). Acetone (Carlo Erba) was used to precipitate grafted depolymerized natural rubber. Modified diglcidyl ether of bishenol-A with epoxy equivalent weight of 175-195 g/equiv (YD 535) and modified aliphatic amine (TH 7256) were supplied by Science International Co., Ltd.

Preparation of Depolymerized Natural Rubber (DNR): Natural rubber latex was diluted by deionized water to a concentration of 5% wt in a 1 liter reaction flask, followed by the addition of MEK and $K_2S_2O_8$ respectively. The latex was adjusted to about pH 9 with 10% KOH and then stirred at 70°C in water bath for 24 hours under a flowing air. At the end of reaction, the reaction mixture was coagulated by 1%

$CaCl_2$ at ambient temperature. The coagulated substance was dissolved in hexane. The resulting solution was purified two times by the re-precipitation method using methanol, followed by vacuum drying at 60°C until weight is constant.

Preparation of Grafted Depolymerized Natural Rubber (GDNR): DNR were dissolved in toluene and heated to 80°C with stirring under a flowing nitrogen atmosphere. After complete dissolution of DNR, monomer mixture of MMA/GMA (90/10 w/w) in an amount of 30% based on rubber content were added. This was followed by the addition of free radical initiator, AIBN. The reaction was continued for 2 h. At the end of reaction, the graft copolymers were precipitated by adding acetone at room temperature. After thoroughly washing with acetone, the graft copolymers were transferred to a vacuum oven at 60°C until weight is constant.

Preparation of the Blends: GDNR (0, 1, 2 or 3 phr) were dissolved completely in curing agent. The stoichiometric amount of epoxy resin was added into the mixture under a stirring. After completely mixed, the mixture was degassed for 15 min and then the mixture was poured into a steel rectangular mould previously coated with releasing agent. The mould was left at room temperature for 24 h. After that, each specimen was cut and polished with a sandpaper. Finally, the specimens were post-cured at 60°C for 12 h in a mechanical convection oven.

Material Characterization: Molecular structure of DNR and GDNR was analyzed by nuclear magnetic resonance spectroscopy in a 300 MHz spectrometer (Varian model Inova 300) at 30°C with deuterated chloroform as a solvent.

Tensile properties of the pure epoxy and the blends were tested according to ASTM D 5083-96 using a universal testing machine (Instron model 5565) with a crosshead speed of 5 mm/min. Five specimens of each material were tested and average values were reported.

Izod unnotched impact tests of the pure epoxy and the blends were tested according to the ASTM D 256, method A, using a basic pendulum impact tester (Atlas model BPI). Ten specimens were tested on each sample. The impact strength was calculated and reported.

Results and Discussion

Graft Copolymerization: The backbone polymer of cis-1,4-polyisoprene was grafted with the methyl methacrylate (MMA) and glycidyl methacrylate (GMA) monomers. To confirm the occurrence of graft copolymers, the ^{1}H-NMR spectra of DNR, grafted DNR and poly(methyl methacrylate)-co-poly(glycidyl methacrylate), PMMA-co-PGMA are compared in Figure 1. The unsaturated methyne proton of NR shows a singlet resonance signal at 5.12 ppm. The methoxy proton of the acrylic group of the MMA unit appears at 3.60 ppm. The peak at 3.12 ppm is due to the methyne proton of the epoxy group of GMA. The methylene protons of the epoxy group of GMA unit show signals at 2.65 and 2.85 ppm. The results confirmed that DNR backbones were grafted with MMA. However, the signal at 3.16 ppm was very low and there was no sign of GMA attached to DNR backbone.

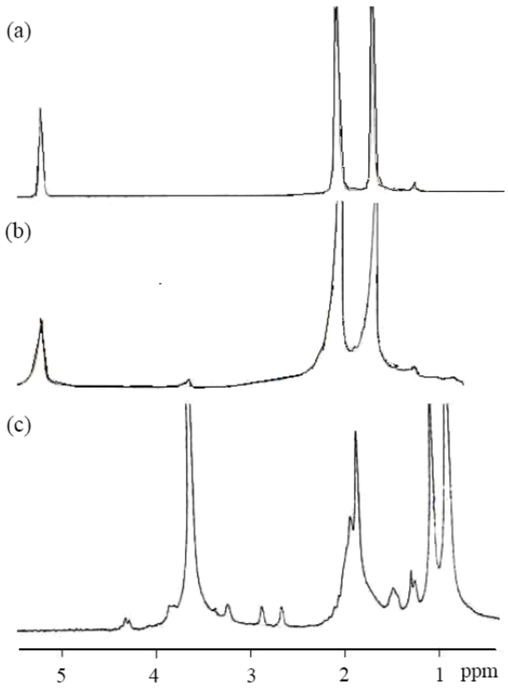

Figure 1. ^{1}H-NMR spectra of polymers: (a) depolymerized natural rubber; (b) grafted depolymerized natural rubber and (c) PMMA-co-PGMA

Izod unnotched impact strength: Izod unnotched impact strength of pure epoxy, DNR/epoxy blends and GDNR/epoxy blends are shown in Figure 2.

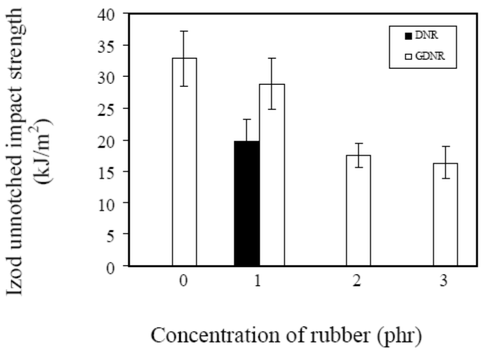

Figure 2. Impact strength of (G)DNR/epoxy resin blends

For the blends containing 1 phr of rubber, the impact strength of GDNR/epoxy blend was higher than that of the DNR/epoxy blend. This may be attributed to the grafted MMA onto DNR backbone which confirmed by ^{1}H-NMR analysis. However, the impact strength of GDNR/epoxy blends was lower than that of pure epoxy resin. This could be because the grafting level was not high enough to improve interfacial adhesion between rubber particles and matrix. Also, the impact strength decreased with increasing rubber content. This might be due to an increase in poor interfacial adhesion between rubber particles and epoxy resin which might possibly act as stress concentrators.

Tensile properties: Figure 3 shows that elongation at break of GDNR/epoxy blends was slightly higher than that of pure epoxy resin. This might be because some of GDNR molecularly dissolved into epoxy matrix. It was assumed that the rubber component exhibited a ductile deformation which contributed to this elongation [8].

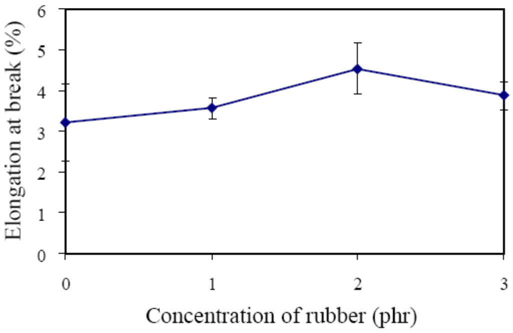

Figure 3. Elongation at break of GDNR/epoxy resin blends

There was no significant change in tensile strength, as shown in Figure 4.

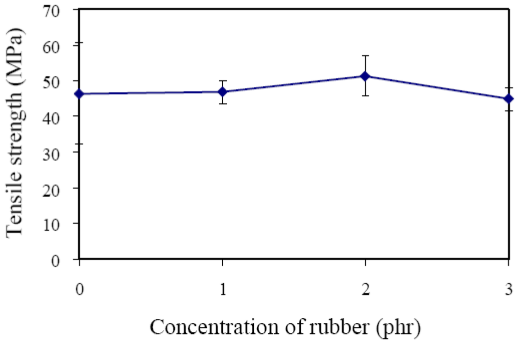

Figure 4. Tensile strength of GDNR/epoxy resin blends

As expect, the tensile modulus gradually decreased with increasing GDNR content as shown in Figure 5. A decrease of modulus could be due to the effect of the softy segment structural of GDNR.

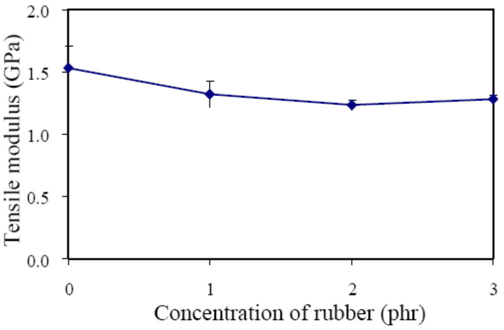

Figure 5. Tensile modulus of GDNR/epoxy resin blends

Conclusions

^{1}H-NMR spectrum of grafted DNR confirmed that DNR backbones were grafted with MMA. For the blends comprising 1 phr of rubber, the impact strength of GDNR/epoxy resin blends was higher than that of the blend containing DNR. However, the impact strength of GDNR/epoxy blends was lower than that of pure epoxy resin. The impact strength and modulus decreased when the concentration of rubber increased. Elongation at break slightly increased with an increase of rubber content.

Acknowledgements

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[Paper ID222] EFFECTS OF TYPE AND CONCENTRATION OF INITIATOR ON GRAFTING OF ACRYLIC MONOMER ONTO DEPOLYMERIZED NATURAL RUBBER

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ABSTRACT

Highly crosslinked epoxy resin for engineering applications is normally stiff but brittle. Therefore, many attempts have been made to improve its toughness. Nowadays, several studies have been done on toughening epoxy resin using natural rubber (NR) because it is abundant and comes from renewable resource. In the present work, NR was subjected to depolymerize in order to achieve molecular dispersion of NR in epoxy matrix. Depolymerized natural rubber (DNR) was prepared by adding a carbonyl compound to natural rubber latex solution and subjecting the mixture to air oxidation in the presence of a radical forming agent at 70°C [1]. In addition, the interfacial adhesion between rubber and matrix must be present to achieve a significant increase in toughness. Hence, DNR was further functionalized by grafting with monomer mixture of methyl methacrylate (MMA)/glycidyl methacrylate (GMA) (90/10 wt/wt%) in an amount of 50% based on rubber content. Solution polymerization was used to graft such monomers using 2 h reaction times at a reaction temperature of 80°C. Two types of initiator used were benzoyl peroxide (BPO) and azo-bis-isobutyronitrile (AIBN). The amounts of initiator in the grafting process were 1, 2, and 3 parts per hundred of DNR. Effects of type and concentration of initiator on grafting efficiency of MMA/GMA monomer mixture onto depolymerized natural rubber were studied by proton nuclear magnetic resonance (^{1}H-NMR) analysis. The molecular weight of DNR was characterized by gel permeation chromatography (GPC). The results indicated good evidence for the formation of graft copolymers in the presence of both initiators, AIBN or BPO. However, the amounts of grafted MMA/GMA on DNR backbone using BPO was higher than those on DNR backbone using AIBN.

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Mechanical Properties of Modified Natural Rubber/Epoxy Resin Blends

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Abstract

The aim of this research was to improve toughness of bisphenol A type epoxy resin by blending with depolymerized natural rubber (DNR) and grafted depolymerized natural rubber (GDNR). GDNR was prepared by grafting DNR with monomer mixture of methyl methacrylate (MMA)/glycidyl methacrylate (GMA) (90/10 wt/wt%). Azo-bis-isobutyronitrile (AIBN) was employed as an initiator. The amounts of DNR and GDNR in the blends were 1, 2 and 3 phr. The number average molecular weight (Mn) of DNR was 64,154 g/mol. The results from proton nuclear magnetic resonance (^{1}H-NMR) analysis showed evidence for the formation of graft copolymers onto the DNR backbone. Flexural and impact tests were performed to observe mechanical behaviour of neat epoxy resin and the blends.

Introduction

Toughening of epoxy resins has been the subject of intense research interest during the last two decades. One of the most successful methods is blending with synthetic reactive liquid elastomers.[1] Nowadays, there are attempts to use natural rubber because it is abundant and comes from renewable resource.[2-3] Nevertheless, due to non-polar nature of NR, interfacial adhesion between NR and epoxy resin is weak. In order to achieve an efficient stress transfer between the rubber and the matrix, the rubber must have functional groups. In this work, DNR and GDNR were used as a toughening agent for epoxy resin.

Material and methods

DNR was prepared following Tanaka, et al.[4] Molecular weight of DNR was calculated using gel permeation chromatography (GPC). GDNR was prepared in toluene at 80°C for 2 h. The monomer mixture of MMA/GMA in an amount of 20% based on rubber content and AIBN of 2 phr were used. The GDNR were characterized using ^{1}H-NMR. In the preparation of the blends, rubbers (DNR or GDNR) were mixed with epoxy resin using mechanical stirrer of 500 rpm for 1 h. Thereafter, the blends were cured using polyamide (Luckamide®) at room temperature for 6 h and then post cured at 120°C for 2 h. The obtained samples were characterized for the flexural and impact properties.

Results and Discussion

^{1}H-NMR spectra of DNR and GDNR are shown in Figure 1.

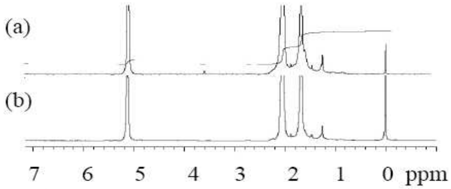

Figure 1: ^{1}H-NMR spectra of polymers: (a) GDNR; (b) DNR

The methoxy proton of the acrylic group of the MMA unit appears at 3.60 ppm. The signal at 2.65 and 2.85 ppm may be attributed to the methylene protons of the epoxy group of GMA. Mn and molecular weight distribution (MWD) of DNR were 64,154 g/mol and 2.329, respectively.

The blends containing 1 phr of rubber showed the highest impact strength [Figure 2]. Impact strength of the blends tended to decrease with increasing rubber content. In addition, the impact strength of the blends containing 3 phr of rubber was lower than that of neat epoxy. This could be due to rubber aggregation. The impact strength of GDNR/epoxy blends seemed to be higher than that of the DNR/epoxy blends. The grafted monomers may improve the interfacial adhesion between rubber and matrix.

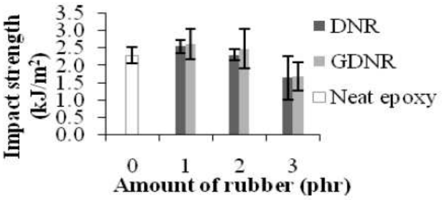

Figure 2: Impact strength of neat epoxy, DNR/epoxy blends and GDNR/epoxy blends

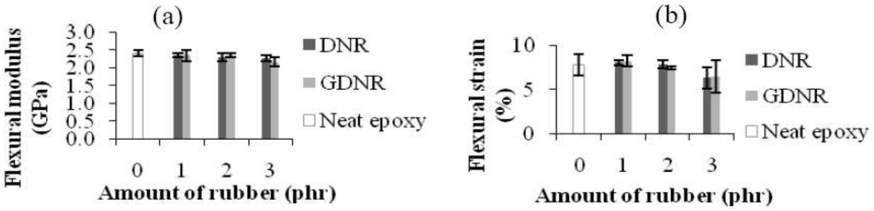

Figure 3: Flexural modulus (a) and strain (b) of neat epoxy, DNR/epoxy blends and GDNR/epoxy blends

The addition of rubber into epoxy slightly brought down flexural modulus as can be seen in Figure 3 (a). This is not unusual because rubber has low modulus. The flexural strain, in Figure 3 (b), of the blends containing 1 phr of rubber was higher than that of neat epoxy. This showed that the rubber modified epoxy has undergone higher percentage of strain (ductile deformation), which will contribute in enhancing the toughness property of the epoxy resin.

Conclusions

The number average molecular weight (Mn) of DNR was 64,154 g/mol. ^{1}H-NMR spectrum of grafted DNR confirmed that DNR backbones were grafted with MMA and GMA. The blends containing 1 phr of rubber showed the highest impact strength and flexural strain. As expected, flexural modulus of the blends was lower than that of neat epoxy. The interfacial adhesion between rubber and matrix has effect on toughness of the blends.

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BIOGRAPHY

Ms. Natkrita Prasoetsopha was born on March 17, 1985 in Ratchaburi, Thailand. Her family has five people. Her mother is Montha Prasoetsopha. She has one elder sister and two elder brothers. She finished primary school from Damnoenvithaya School and secondary school from Saithamachan School. After that, she continued her study in faculty of science at Kasetsart University (KU), Bangkhen, Bangkok and earned her Bachelor's degree in Chemistry in 2007. While she studied at Kasetsart University, she was a member of Rotaract Club. During her graduate study, she got a research assistant scholarship from the Center of Excellence for Petroleum, Petrochemical and Advanced Materials, Chulalongkorn University, Thailand. Her research was about "Studied of modified natural rubber/epoxy resin blend". Several parts of her work were presented at Pure and Applied Chemistry International Conference (PACCON 2009), Phitsanulok, Thailand, at the International Conference on Advance in Materials and Processing Technologies (AMPT 2009), Kuala Lumper, Malaysia and at 11th Pacific Polymer Conference 2009 (PPC11), Cairns, Australia.