National Library of Canada
Bibliothèque nationale du Canada

Canadian Theses Service
Service des thèses canadiennes

Ottawa, Canada
K1A 0N4

NOTICE

The quality of this microform is heavily dependent upon the quality of the original thesis submitted for microfilming. Every effort has been made to ensure the highest quality of reproduction possible.

If pages are missing, contact the university which granted the degree.

Some pages may have indistinct print especially if the original pages were typed with a poor typewriter ribbon or if the university sent us an inferior photocopy.

Reproduction in full or in part of this microform is governed by the Canadian Copyright Act, R.S.C. 1970, c. C-30, and subsequent amendments.

AVIS

La qualité de cette microforme dépend grandement de la qualité de la thèse soumise au microfilmage. Nous avons tout fait pour assurer une qualité supérieure de reproduction.

S'il manque des pages, veuillez communiquer avec l'université qui a conféré le grade.

La qualité d'impression de certaines pages peut laisser à désirer, surtout si les pages originales ont été dactylographiées à l'aide d'un ruban usé ou si l'université nous a fait parvenir une photocopie de qualité inférieure.

La reproduction, même partielle, de cette microforme est soumise à la Loi canadienne sur le droit d'auteur, SRC 1970, c. C-30, et ses amendements subséquents.

NL 339 (r. 88/04) c

Canada

SYNTHETIC POLYMER (EPOXY) - LIGNIN POLYBLENDS AS STRUCTURAL ADHESIVES

JIASHU WANG

A THESIS

IN

THE CENTRE FOR BUILDING STUDIES

PRESENTED IN PARTIAL FULFILMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY AT
CONCORDIA UNIVERSITY
MONTREAL, QUEBEC, CANADA
JANUARY 1992

ISBN 0-315-73663-1

ABSTRACT

SYNTHETIC POLYMER (EPOXY) - LIGNIN POLYBLENDS AS STRUCTURAL ADHESIVES

JIASHU WANG, Ph.D.
CONCORDIA UNIVERSITY, 1992

Synthetic polymer (Epoxy) - Lignin polyblends as structural adhesives with significantly improved adhesive properties, durability and cost advantages have been developed by an effective and economical blending technique as an alternative approach to the current chemical synthetic methods. This research project is also of great significance in cultivating a market for lignin, a highly underutilized waste and byproduct of the pulp and paper industry which also affects the cleanness of the environment.

Some important factors (curing temperature, lignin content and others) which influence the adhesive joint shear strength of Epoxy-Lignin adhesives and the influence of different types of lignin (various sources), epoxy systems, fillers, third polymeric components and organofunctional silane coupling agents have been studied.

As a novel adhesive, its surface energy parameters (contact angle, surface free energy, interfacial free energy, speading coefficient, Girifalco-Good's interaction parameter and work of adhesion) have been experimentally determined. A direct correlation between the obtained surface thermodynamic parameters and the determined adhesive joint shear strength has been established.

Differential scanning calorimetry, Dynamic mechanical analysis and Nuclear magnetic resonance techniques were performed on EP-L polyblends; they clearly demonstrate that thermally cured Epoxy-Lignin polyblends with up to 20% lignin are miscible systems. Research techniques, including FTIR, titration, kinetics, extraction, and UV spectroscopy, demonstrate that lignin chemically reacted with the epoxy-polyamine network via unreacted amine groups of the hardener during the thermal cure of epoxy-lignin polyblends. These findings not only reveal the morphology feature and chemical interaction mechanism of these new EP-L polyblends, but also emphasize their value of application in various material fields such as adhesives, coatings, structural plastics, composites, mortars and injection resins.

ACKNOWLEDGEMENTS

The author is grateful to his thesis supervisor, Dr. Dorel Feldman, Professor at the Centre for Building Studies, for his supervision, guidance, and encouragement throughout the course of this research work.

The author wishes to thank Mrs. Dorina Banu, research associate, and Dr. Christina Luchian, postdoctoral fellow, and Dr. M.A. Lacasse for the co-works and helpful suggestions.

The author is grateful to Dr.Almeria Natansohn, Associate Professor at Queen's University, for having completed the NMR portion of this study.

A note of thanks is extended to the technicians who helped in this endeavour and in particular, Mr. Joseph Hrib, Mr. Joseph Zilka and Hans Obermeir.

The author would also like to express his appreciation to the Natural Science and Engineering Research Council of Canada for financial support.

Thanks are also extended to Ciba-Geigy Co. of Canada and Domtar Research Centre for providing some of the materials used in this study as well as some of its analysis.

A very special note of thanks is extended to the author's wife, Huiwen, and his daughter, Liming, for their continued support and encouragement throughout this endeavour.

THIS WORK IS DEDICATED TO MY WIFE

HUIWEN

FOR HER CONSTANT LOVE, SUPPORT AND PATIENCE

TABLE OF CONTENTS

PAGE No.

1. GENERAL INTRODUCTION 1

1.1 PURPOSES AND OBJECTIVES OF RESEARCH 1

1.2 OUTLINE OF THESIS 5

1.3 USE AND SIGNIFICANCE OF EPOXY ADHESIVES IN CONSTRUCTION 8

1.3.1 CHEMISTRY OF EPOXY RESINS 8

1.3.2 EPOXY STRUCTURAL ADHESIVES 14

1.4 LIGNIN AND LIGNIN DERIVATIVES 19

1.5 POLYBLENDING 22

2. LITERATURE SURVEY OF POLYMER-LIGNIN SYSTEMS 26

2.1 DEVELOPMENT OF POLYMER-LIGNIN BUILDING MATERIALS 26

2.1.1 ENGINEERING PLASTICS 26

2.1.2 ADHESIVES 28

2.1.3 FOAMS AND OTHERS 35

2.2 FUNDAMENTAL ASPECTS OF POLYMER-LIGNIN SYSTEMS 38

2.3 RESEARCH RELATED TO EP-L SYSTEMS 45

3. THE DEVELOPMENT OF EP-L POLYBLENDS AND THEIR ADHESIVE PROPERTIES 50

3.1 INTRODUCTION 50

3.2 CHARACTERIZATION OF COMPONENTS 51

3.1.1 EPOXY 51

3.1.2 LIGNIN 51

3.3 PREPARATION OF EP-L POLYBLENDS 53

3.4 FACTORS WHICH INFLUENCE THE ADHESIVE JOINT SHEAR STRENGTH OF EP-L ADHESIVES 53

3.4.1 SHEAR STRENGTH TEST 53

3.4.2 THE EFFECT OF CURING TEMPERATURE ON ADHESIVE JOINT SHEAR STRENGTH 54

3.4.3 THE EFFECT OF CURING SCHEDULE ON THE ADHESIVE JOINT SHEAR STRENGTH 56

3.4.4 THE EFFECT OF THE AMOUNT OF LIGNIN ON ADHESIVE JOINT SHEAR STRENGTH 58

3.5 ECONOMICS EVALUATION 58

3.6 SUMMARY 62

4. MISCIBILITY 63

4.1 INTRODUCTION 63

4.2 POLYMER-POLYMER MISCIBILITY AND GLASS TRANSITION TEMPERATURE 65

4.3 MISCIBILITY STUDY BY DSC 68

4.4 MISCIBILITY STUDY BY DMA 70

4.5 MISCIBILITY STUDY BY NMR 81

4.6 SUMMARY 84

5. INTERACTION BETWEEN EPOXY-POLYAMINE NETWORK AND LIGNIN 86

5.1 INTRODUCTION 86

5.2 FOURIER TRANSFORM INFRARED SPECTROSCOPY 86

5.2.1 PRINCIPLE OF FTIR 86

5.2.2 SPECTRA OF EPOXY AND LIGNIN 89

5.2.3 SPECTRA OF LIGNIN-AMINE BLEND 93

5.2.4 SPECTRA OF LIGNIN-EPOXY-POLYAMINE BLENDS 96

5.2.5 SUMMARY OF FTIR STUDY 99

5.3 QUANTITATIVE DATA CONCERNING THE REACTIVITY OF LIGNIN TOWARDS THE POLYAMINE HARDENER 99

5.4 KINETICS 101

5.4.1 THEORY AND CALCULATION (BORCHARDT AND DANIELS PROGRAM) 101

5.4.2 EXPERIMENT AND RESULTS 103

5.5 EXTRACT OF EP-L POLYBLENDS AND DETERMINATION OF THE BONDED LIGNIN 105

5.5.1 SCHEME 105

5.5.2 EXTRACTION 105

5.5.3 UV SPECTROSCOPY 106

5.5.4 EXTRACTIBILITY OF LIGNIN FROM EP-L POLYBLENDS 106

5.6 SUMMARY 110

6. EP-L BLENDS MODIFIED BY SILANE COUPLING AGENTS 112

6.1 INTRODUCTION 112

6.2 MATERIALS AND PROCEDURES 114

6.2.1 MATERIALS 114

6.2.1.1 EPOXY POLYMER 114

6.2.1.2 LIGNIN 114

6.2.1.3 SILANES 114

6.2.2 PREPARATION OF POLYBLENDS 115

6.2.3 SHEAR STRENGTH TEST 116

6.2.4 WATER RESISTANCE AND UV EXPOSURE 116

6.3 SILANES AS EP-L BLEND ADDITIVE 116

6.3.1 SILANE CONCENTRATION 116

6.3.2 EFFECT ON ADHESIVE JOINT SHEAR STRENGTH 118

6.4 WATER RESISTANCE 121

6.5 UV EXPOSURE 125

6.6 SUMMARY 125

7. POLYMER SURFACE AND ADHESION 130

7.1 INTRODUCTION 130

7.2 POLYMER SURFACE BEHAVIOUR 132

7.2.1 THEORY AND CALCULATION 132

7.2.2 RESULTS 134

7.3 RELATIONSHIPS BETWEEN CALCULATED WORK OF ADHESION AND EXPERIMENTAL ADHESIVE JOINT SHEAR STRENGTH 137

7.3.1 THEORY AND CALCULATIONS 137

7.3.2 RESULTS 139

7.4 SUMMARY 146

8. EFFECTS OF VARIOUS COMPONENTS ON ADHESIVE PROPERTIES, AND THE DURABILITY OF EP-L ADHESIVES 147

8.1 INTRODUCTION 147

8.2 COMPONENTS 148

8.2.1 EPOXY PREPOLYMERS AND HARDENERS 148

8.2.2 LIGNINS 148

8.2.3 FILLERS 152

8.2.4 THIRD POLYMERIC COMPONENTS 155

8.3 INFLUENCE OF VARIOUS TYPES OF LIGNIN 155

8.4 INFLUENCE OF LIGNIN MOLECULAR WEIGHT 157

8.5 INFLUENCE OF VARIOUS TYPES OF EPOXY SYSTEMS 158

8.6 INFLUENCE OF DIFFERENT HARDENERS 162

8.7 MINERAL FILLERS IN EP-L ADHESIVES 164
8.8 THIRD POLYMERIC COMPONENT IN EP-L ADHESIVES 166
8.9 WEATHERABILITY 168
8.10 PHOTOSTABILITY 168
8.11 SUMMARY 171

9. CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE RESEARCH 173
9.1 CONCLUSIONS 173
9.2 RECOMMENDATIONS FOR FUTURE RESEARCH 177

REFERENCES 179

APPENDIX 1

STANDARD DEVIATION DATA OF ADHESIVE JOINT SHEAR STRENGTH IN FIGURES 192

APPENDIX 2

STANDARD DEVIATION DATA OF CONTACT ANGLE IN TABLE.7.1 211

LIST OF FIGURES

FIG. No. PAGE No.

1.1 Epoxy Group 10

1.2 General Formula For Epoxy 10

1.3 Reaction between An Epoxy Resin and A Primary Diamine 12

1.4 Basic Structures in Soft Wood Lignin Shown with 16 Phenyl Propane Unite [32] 20

3.1 Effect of Curing Temperature on Adhesive Joint Shear Strength of EP-L40 [2] 55

3.2 Adhesive Joint Shear Strength of EP & EP-L20 vs. Delaying of Thermal Curing [2] 57

3.3 Effect of the Amount of Lignin on Adhesive Joint Shear Strength Of EP-L [2] 59

3.4 Adhesive Joint Shear Strength and Related Cost of EP-L and the Control EP [6] 61

4.1 The Effect of Thermal Curing on Adhesive Joint Shear Strength of EP and EP-L20 64

4.2 DSC Curve of Epoxy 71

4.3 DSC Curve of Lignin (Tomlinite) 71

4.4 Effect of Lignin Amount on Tg of EP-L Blends 72

4.5 The Relation Between Lignin Amount and the First Tg of EP-L 73

4.6 Tan δ (DMA) vs. Temperature For EP and EP-L [2] 77

4.7 DMA Damping Signals vs. Temperature for EP and EP-L Polyblends [2] 79

4.8 DMA Damping Signals vs. Temperature for EP and EP-L Polyblends Previously Cured for 2 h at 100°C [2] 79

4.9 $T_{1\rho}H$ Signal for EP and L in control Specimens and EP-L Polyblends [2] 83

5.1 The FTIR Spectrum of Thermally Cured Epoxy (CA1200) 90

5.2 The FTIR Spectrum of Kraft Lignin (Tomlinite) 92

5.3 Difference FTIR Spectra of Lignin-Polyamine (1:1.08) (Before and After Thermal cure) [1] 95

5.4 Difference FTIR Spectra of EP-L Polyblends, EP control Cured at Room Temperature [1] 98

5.5 Difference FTIR Spectra of EP-L Polyblends, EP Control Thermally Cured [1] 98

5.6 DSC Scans for Lignin-Polyamine Blends [1] 104

5.7 UV Spectrum of Lignin [1] 107

5.8 UV Calibration Curve for Lignin at 277 nm [1] 108

5.9 Extractibility of Lignin from the Thermally ured EP-L Polyblends [1] 109

6.1 Effect of Silane Concentration on Adhesive Joint Shear Strength of EP-L10-A1110 117

6.2 Effect of Silanes on Adhesive Joint Shear Strength of EP and EP-L10 [3] 119

6.3 Effect of Silane on Water Resistance of EP-L10 (immersion in water at 23°C for 630 h) [3] 123

6.4 Water Resistance of EP, EP-L10 and EP-L10-A187 (immersion in water at 23°C for 630 h) 124

6.5 Effect of Silane on UV Resistance of EP-L10 (400 W lamp, 15 cm distance, 700 h) 126

6.6 UV Resistance of EP, EP-L10 and EP-L10-Silane (400 W lamp, 15 cm distance, 700 h) 127

7.1 Calculated Work of Adhesion Compared With Adhesive Joint Shear Strength [3] 140

7.2 Interfacial Free Energy Compared With Adhesive Joint Shear Strength [3] 142

7.3 Interaction Parameter (adhesive/Al) Compared With Adhesive Joint Shear Strength [3] 143

8.1 The Molecular Weight Distribution of Tomlinite Lignin and of its Fractions [6] 153

8.2 Influence of Different Lignins on Adhesive Joint Shear Strength of EP-L [6] 156

8.3 Relation Between Mw of Lignin and the Adhesive Joint Shear Strength of EP-L10 [6] 159

8.4 Influence of Different EP on Adhesive Joint Shear Strength of EP-L [6] 161

8.5 Influence of Different Hardeners on Adhesive Joint Shear Strength of EP-L [6] 163

8.6 Influence of Fillers on Adhesive Joint Shear Strength of EP-L20 [6] 165

8.7 Influence of PVC or Phenoxy Component on the Adhesive Joint Shear Strength of EP-L20 [6] 167

8.8 The Adhesive Joint Shear Strength of EP and EP-L Blends Before and After Accelerated Weathering 169

8.9 The Adhesive Joint Shear Strength of EP and EP-L20 Blends Before and After UV Exposure 170

LIST OF TABLES

TABLE No.		PAGE No.
3.1	Chemical and Physical Characteristics of Tomlinite	52
3.2	Comparison of the Adhesive Joint Shear Strength & Related Costs of EP-L Polyblends	60
5.1	Amine Number Data for the L-H Blends [1]	100
7.1	Comparison of Surface Parameters of EP, EP-L10 and EP-L10-A187 [3]	135
7.2	Calculated W_{a1} Compared with Adhesive Joint Shear Strength in Water [3]	145
8.1	Characteristics of the Epoxy Prepolymers [6]	149
8.2	Characteristics of the Hardeners [6]	149
8.3	Physical Characteristic of Lignins [6]	150
8.4	Fractionation Yields, Average Molecular Weights and Polydispersity of Tomlinite Lignin and its Fractions [6]	154

LIST OF ABBREVIATIONS AND SYMBOLS

Al	ALUMINUM
AT	INDULIN AT LIGNIN
B-CWL-1	HIGH MOLECULAR WEIGHT SOLVOLYSIS
B-CWL-2	LOW MOLECULAR WEIGHT SOLVOLYSIS
cP	CENTIPOISE
CEHPL	CHAIN-EXTENDED HYDROXYPROPYL LIGNIN
COV	COEFFICIENT OF VARIATION
$d\alpha/dt$	REACTION RATE (1/sec)
DGEBA	DIGLYCIDYL ETHER OF BISPHENOL A
DMA	DYNAMIC MECHANICAL ANALYSIS
DSC	DIFFERENTIAL SCANNING CALORIMETRY
E	ACTIVATION ENERGY (J/mole)
EP	EPOXY
EP-L	EPOXY-LIGNIN BLENDS
EP-L5	EPOXY-LIGNIN (5% BY WEIGHT) BLENDS
EP-L10	EPOXY-LIGNIN (10% BY WEIGHT) BLENDS
EP-L15	EPOXY-LIGNIN (15% BY WEIGHT) BLENDS
EP-L20	EPOXY-LIGNIN (20% BY WEIGHT) BLENDS
EP-L25	EPOXY-LIGNIN (25% BY WEIGHT) BLENDS
EP-L30	EPOXY-LIGNIN (30% BY WEIGHT) BLENDS
EP-L40	EPOXY-LIGNIN (40% BY WEIGHT) BLENDS
EP-L50	EPOXY-LIGNIN (50% BY WEIGHT) BLENDS
equiv.	EQUIVALENT
EU	EUCALIN LIGNIN
FTIR	FOURIER TRANSFORM INFRARED SPECTROSCOPY

G	DYNAMIC MODULUS
G′	STORAGE MODULUS
G′′	LOSS MODULUS
GPC	GEL PERMEATION CHROMATOGRAPHY
h	HOURS
HDPE	HIGH DENSITY POLYETHYLENE
HPL	HYDROXYPROPYL-LIGNIN
IR	INFRARED SPECTROSCOPY
k(T)	SPECIFIC RATE CONSTANT AT TEMPERATURE T (1/sec)
L	LIGNIN
LF	LIGNIN-BASED PHENOL RESIN
L-H	LIGNIN-HARDENER BLEND
LPF	LIGNIN-BASED PHENOL RESIN
min	MINIMUM
MPa	MEGAPASCAL
Mn	NUMBER AVERAGE MOLECULAR WEIGHT
Mw	WEIGHT AVERAGE MOLECULAR WEIGHT
MW	MOLECULAR WEIGHT
n	REACTION ORDER (DIMENSIONLESS)
NMR	NUCLEAR MAGNETIC RESONANCE
PBDG	POLYBUTADIENE GLYCOL
PEG	POLYETHYLENE GLYCOL
PP	POLYPROPYLENE
PU	POLYURETHANE
PVC	POLYVINYL CHLORIDE
R	GAS CONSTANT (8.314 J/mole·K)
RF	RESORCINOL PHENOL RESIN
S_c	SPREADING COEFFICIENT

SEL	STEAM EXPLODED LIGNIN
T	TEMPERATURE
$T_{1p}H$	ROTATING FRAME PARAMETER
Tan δ	MECHANICAL LOSS FACTOR
Tg	CLASS TRANSITION TEMPERATURE
TO	TOMLINITE LIGNIN
UV	ULTRAVIOLET SPECTROSCOPY
Var(X)	VARIANCE
vs.	VERSUS
W_a	WORK OF ADHESION IN AIR
W_{al}	WORK OF ADHESION IN WATER
wt.	WEIGHT
X	MEAN VALUE
Z	PRE-EXPONENTIAL FACTOR OR ARRHENIUS FREQUENCY FACTOR (1/sec)

LIST OF GREEK SYMBOLS

α	FRACTIONAL CONVERSION
γ_s	SOLID SURFACE FREE ENERGY
γ_l	LIQUID SURFACE FREE ENERGY
γ_{sl}	INTERFACIAL FREE ENERGY BETWEEN A SOLID AND A LIQUID
θ	CONSTANT ANGLE
γ_c	CRITICAL SURFACE ENERGY
γ^d	DISPERSION COMPONENT OF SURFACE FREE ENERGY
γ^p	POLAR COMPONENT OF SURFACE FREE ENERGY
σ_x	STANDARD DEVIATION

CHAPTER 1

GENERAL INTRODUCTION

1.1 PURPOSES AND OBJECTIVES OF RESEARCH

It has long been the object of researchers to commercially utilize lignin (L). Although lignin is currently highly underutilized, it has the potential of becoming a major source of polymer-based products.

Lignin is a natural polymer which acts as a cementing agent matrix of cellulose fibres in the woody structure of plants. It is one of the principal constituents of wood (around 25%) and is the second most abundant natural polymer after cellulose. It is non toxic and has good weatherability and good resistance to microorganisms.

Most lignin applications are based on technical lignins, i.e. lignosulphonates and kraft lignin, which are separated during pulping processes, and hydrolysis lignin, which is obtained during wood acidic hydrolysis. The sulphate and soda pulping processes result in spent liquors, called black liquors, from which kraft lignins may be obtained. This byproduct may be used as a source of fuel, as a source of low molecular weight chemicals or the basic polymer from which more useful high molecular weight products may be derived.

The basic chemical components of lignin (primarily syringyl, guaiacyl and p-hydroxy phenol) are bonded together by a set of linkages to form a very complex matrix. This matrix comprises a variety of functional groups, such as hydroxyl, methoxyl and carbonyl, which impart a high polarity to the lignin macromolecule. Due to these characteristics, lignin appears to be an extremely promising material in the field of organic fillers or as a chemical component in polyblends.

Epoxy polymer (EP) systems provide excellent strength, chemical resistance, adhesive and electrical properties. This combination of superior properties, coupled with the variety and breadth of applications, has made these systems superior to many other polymeric materials. Their applications vary from electronic encapsulation to protective coatings, structural plastics and adhesives.

In the building and construction industry, epoxy systems find a variety of applications as adhesives, mortars, injection resins, composite materials and coatings. Although today epoxy adhesives represent a relatively small part of the total adhesive market for building and construction, they are one of the best structural adhesives available where high strength and durability are critical. The main hindrance is their high price, which makes them less competitive in building applications. They are in need of modification to decrease their cost while maintaining or improving their performance properties.

Researchers have made an attempt to prepare epoxy-lignin

(EP-L) systems through chemical synthetic methods, which usually consist of high temperature chemical processes or catalytic reactions. Lignin utilization is possible but it usually requires chemical modification. However, problems facing lignin modification and synthesis of epoxy-lignin include lignin's natural variability, inhomogeneity, and a complex chemical and macromolecular structure making the task of quality control exceedingly difficult. These may be some of the reasons for the difficulties encountered in the production of useful polymeric products from lignin.

In this study, as an alternative to chemical modification of lignin, lignin is directly used, without modification, in a very simple and economical blending process. That is, without any high temperature chemical process or catalytic reaction, the liquid epoxy prepolymer, lignin and hardener or other additives are simply mixed at room temperature.

This study [1-6] shows that the adhesive joint shear strength and durability of these novel EP-L polyblends is significantly improved in comparison with that of the control epoxy adhesive. A significant cost advantage results from the adhesives, since lignin without chemical modification is a very inexpensive commercial byproduct and the blending method used in this study is simple and economical. This is a significant factor in cultivating a market for both lignin and epoxy.

In addition to the various parameters, which affect the adhesive properties of EP-L, being investigated, fundamental research was carried out on these novel EP-L polyblends. In order to establish the morphology, miscibility, chemical interaction mechanism between lignin and the epoxy network, and the surface properties, certain modern research techniques were applied:

- Differential Scanning Calorimetry (DSC);
- Dynamic Mechanical Analysis (DMA);
- Fourier Transform Infrared Spectroscopy (FTIR);
- Ultraviolet Spectroscopy (UV);
- Nuclear Magnetic Resonance (NMR);
- Gel Permeation Chromatography (GPC).
- Contact angle measurement

It is well known that the miscibility is the most important and significant study in the polyblend research field. Scientists want to improve the miscibility of polyblends since the mechanical properties of miscible polyblends are usually superior to these of immiscible ones. Our works [2,4] based on DSC, DMA, NMR techniques clearly demonstrate that thermally cured CA 1200 epoxy-polyamine blends with up to 20% Tomlinite kraft lignin are miscible systems resulting in a significant improvement of adhesive properties. FTIR spectra indicate that a chemical interaction takes place between lignin and polyamire hardener during the thermal cure of EP-L [1,4]. These findings not only reveal the important morphology feature of these new EP-L polyblends, but also emphasize their value of application in various material fields since the fact of miscible morphology may give these new EP-L polyblends vast prospects of application in adhesives, coatings, structural plastics, composite materials, mortars, injection resins and so on.

In conclusion, the general purposes of this study are:

- to help develop more cost effective EP-L adhesives with better adhesive properties by the blending method;
- to aid in cultivating a market for lignin, a highly underutilized polymeric material, readily available from industry as a byproduct.

According to these purposes, the major objectives of the research program are to establish

- the various process parameters which influence the adhesive joint shear strength of EP-L polyblends;
- the effects of various components and additives on adhesive properties and durability of EP-L polyblends;
- the morphology and miscibility of the novel EP-L polyblends;
- the chemical interaction mechanism between lignin and epoxy network.

1.2 OUTLINE OF THESIS

This thesis is subdivided into 10 chapters.

In Chapter 1 (the general introduction), the purposes and objectives of this research are given. Following that, three basic aspects concerning the background of this research project are introduced: (1) epoxy (2) lignin and (3) polyblending.

On the basis of a literature survey of lignin - synthetic polymer system (Chapter 2), the conclusion is that lignin utilization is possible but it requires chemical modification and/or chemical synthetic methods, which creates some technical and economical difficulties. Facing this problem, a significant task is suggested as the purpose of this research: to develop a more useful and cost effective novel EP-L polyblend, without chemical modification of lignin, by a effective and economic blending method.

In order to develop such a new EP-L adhesive, the process factors which influence the adhesive joint shear strength of EP-L are investigated in Chapter 3 [2,4]. This results in the development of novel EP-L adhesives with significant improvement of adhesive joint shear strength up to 178% of the control EP and a cost advantage.

Why is lignin additive able to improve the adhesive properties of EP-L polyblend? How does lignin additive improve the adhesive strength of EP-L polyblend? The answer comes from a systematic investigation concerning morphology and miscibility of EP-L polyblend components (Chapter 4) [2,4], which is the most important and significant topic known in the polyblend research field. The results of DSC, DMA and NMR clearly demonstrate that the thermally cured EP-L blends with up to 20% lignin are miscible systems, resulting in a significant improvement of adhesive properties.

How does the EP-L polyblends with up to 20% kraft lignin transform from immiscible to miscible during thermal curing, resulting in a sixfold increase of adhesive joint shear strength (as mentioned in Chapter 4)? A successful finding [1,4], which may respond to the above question, is revealed by the FTIR technique, chemical titration, curing kinetics, extraction and UV analysis method in Chapter 5. That is, a chemical interaction takes place between lignin and the epoxy-polyamine network through amine groups during thermal cure.

As mentioned above, there are basic studies from Chapters 1 to 5, i.e., general introduction (Chapter 1), literature survey (Chapter 2), EP-L development (Chapter 3) and fundamental research concerning the morphology, miscibility (Chapter 4) and chemical interaction mechanism (Chapter 5). These studies are based on a common EP-L formulation. The following chapters extend this study to various formulations, i.e., different components and additives and discuss their influence on the adhesive properties and durability of EP-L adhesives, as well as the surface properties of EP-L.

In Chapter 6, an organofunctional silane coupling agent is introduced to EP-L blends (2% by weight) and the adhesive joint shear strength of EP-L is improved significantly, as well as its durability to water and UV exposure [3,5].

Analysis of the polymer surface is becoming increasingly important in general studies of adhesive bonding. In Chapter 7, the surface energy analysis, contact angle study, carried out on EP, EP-L and EP-L with silane. The surface thermodynamic parameters are determined. The relationship between the surface thermodynamic parameters and measured adhesive joint shear strength is discussed [3,5].

In Chapter 8 [6], the influence of various lignins, epoxy prepolymers, hardeners, fillers and third macromolecular components on the EP-L adhesive properties, weatherability and photostability are discussed. The improved adhesive joint shear strength resulting from various epoxy-lignin formulations confirms the wide versatility of lignin to epoxy systems, which is of great significance since a rather wide variety of lignins may be used as modifiers of epoxy adhesives and may give these novel EP-L adhesives vast prospects in application.

Finally, conclusions and recommendations are presented in Chapter 9 and references are given.

1.3 USE AND SIGNIFICANCE OF EPOXY ADHESIVES IN CONSTRUCTION

1.3.1 CHEMISTRY OF EPOXY RESINS

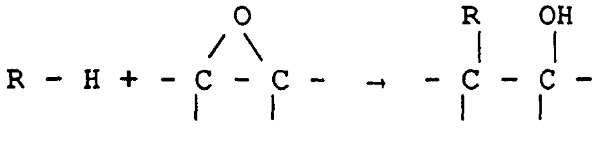
Epoxy resins contain epoxy groups (also called the epoxide, oxirane, or ethoxyline). Epoxy group is a threemember oxide ring. Ethylene oxide is the simplest epoxy group. Fig. 1.1 gives the formula for this compound.

Epoxy resins can be regarded as compounds which contain, on average, more than one epoxy group per molecule. They are cured using a cross-linking agent (also called a curing agent or hardener), to form a three-dimensional network. It is in this cured form that the resins are almost always used; in the uncured non-cross-linked state, they are of limited utility.

The most important group of commercially available resins are based on the diglycidyl ethers of bisphenol A (DGEBA). Nearly 95% of all epoxy resins are made by the interaction of epichlorohydrin and diphenylolpropane. Their general formula is given in Fig.1.2.

The resins will, in general, react with compounds containing active hydrogen atoms, such as phenols, alcohols, thiols, primary and secondary amines, and carboxylic acids. The reactivity of the epoxy group towards any of these curing agents will be different for various resin types, depending upon the electronic environment of the group and steric factors.

In these reactions, the epoxy ring is opened to form an alcohol:



$$R - H + -\underset{|}{C}\overset{\overset{O}{/\;\backslash}}{\;\;}\!\!-\underset{|}{C}- \rightarrow -\underset{|}{\overset{\overset{R}{|}}{C}}-\underset{|}{\overset{\overset{OH}{|}}{C}}-$$

Thus, when a diepoxy (functionality 2) reacts with a substance

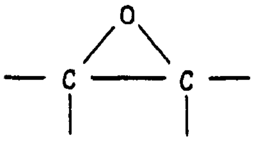


FIG.1.1 EPOXY GROUP

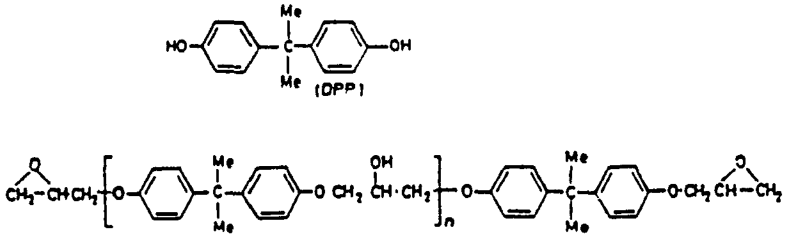


FIG.1.2 GENERAL FORMULA FOR EPOXY

possessing four active hydrogen atoms (functionality 4), a system of functionality 4:2 is created. This produces a cross-linked structure. The hydroxyl groups formed when the epoxy group opens may, in certain circumstances, also react with the epoxy and other groups present. In this case the effective functionality of each epoxy group increases from 1 to 2 and therefore the functionality of the diepoxy compound increases from 2 to 4. Fig.1.3 shows a typical example of curing between an epoxy resin and a primary diamine.

The useful properties of epoxy resins only appear after curing. The curing step transforms the epoxy from a low-molecular-weight prepolymer to a highly crosslinked space network. The network is composed of segments involving both the epoxy unit and the crosslinking agent. Thus, in even the simplest formulation the chemical and physical properties of the cured resin are influenced by the separate chemistries and structures of the diepoxy or polyepoxy monomer and the polyfunctional crosslinking agent. When the molecular weights of both reactants of the cured resin are high enough to provide more than four chain atoms between junction points, the resultant network begins to display the properties of a three-dimensional block copolymer [7]

The cured resins have technologically significant properties such as high mechanical strength and electrical and chemical resistance, as well as the capability of adhering to many substrates.

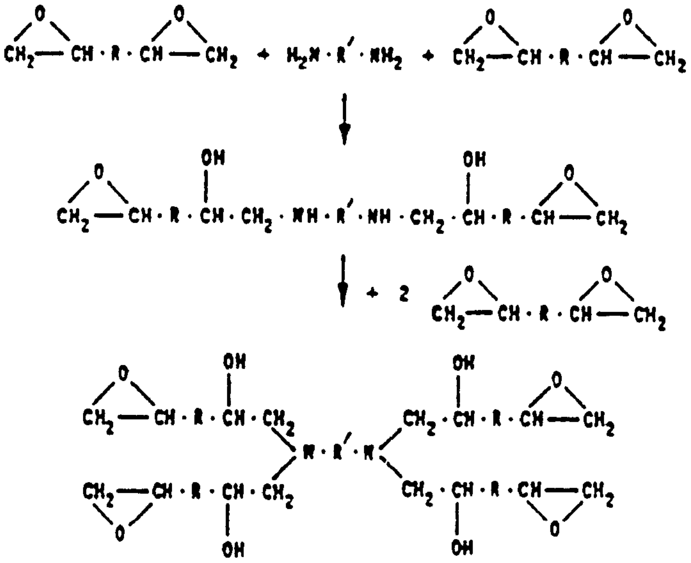


FIG.1.3 REACTION BETWEEN AN EPOXY RESIN AND A PRIMARY DIAMINE

Flexibilisers, used to reduce the generic brittleness of epoxy systems, are divided into two main groups: (1) reactive flexibilisers, that lead to the incorporation of long flexible molecular chains in the system's network and (2) non-reactive plasticisers that lead to unreacted long-chain molecules within the cured system.

Thermoplastics, thermosets and elastomers have been used to modify the properties of epoxy systems. Many modifying polymer resins react chemically with the epoxy polymers forming copolymers, or polymer alloys. These include nylon, vinyl, PVC, polyester, polyurethane, butadiene-acrylonitrile rubber and phenolic resins. Other polymers such as coal-tar pitch and petroleum-derived bitumens are used to alter certain properties and decrease the cost of the epoxy system. These do not react chemically with the epoxy polymers.

Fillers and reinforcements are used to enhance or obtain specific desired properties in an epoxy system, and to reduce material cost. These additives may increase viscosity, surface hardness, impact strength, thermal conductivity and specific gravity. They may also decrease the coefficient of thermal expansion, and shrinkage. Certain fillers could change the electrical and chemical properties. Other additives include cure accelerators, fire retardants and antioxidants.

1.3.2 THE EPOXY STRUCTURAL ADHESIVES

Although epoxy resin technology was initiated in Europe and the United States in the 1920's and early 1930's, modern epoxy resin technology is considered to have began with the patent of Schlack of I.G. Farben [8-10]. In 1934, Schlack mentioned the polyglycidyl ethers of polyphenols that were later acknowledged as resins by Moss in 1937 [11]. In 1936, P. Castan developed a low-melting resin that produced a thermosetting compound when reacted with phthalic anhydride. His patents of 1938 and 1943 describe the production of diglycidyl ethers and esters, and the polymerization of these resins with acid anhydrides. These resins included one based on bisphenol-A and epichlorohydrin [8,9]. In 1946, Ciba of Basel introduced epoxy resin adhesive (Araldite I) at the Swiss Industries Fair[8,12]. Meanwhile in 1939, J.O. Greenlee of Devoe-Reynolds of the United States developed new coating resins through the synthesis of bisphenol-A and epichlorohydrin [9,10]. Shell Chemicals Corporation, after obtaining licenses to Devoe-Reynolds' patents, started marketing a number of liquid and solid epoxy resins. Production of bisphenol-A type resins in the USA rose from a zero base in 1948 to 170 million pounds in 1965 [9,10]. By the late 1960's, at least 25 types of resins were commercially available, including polyfunctional and cycloaliphatic resins, and resins for flame retardancy and flexible coatings [8,9,12]. Since then, there has been a rapid increase to

400,000 tons (1985) in the world production of epoxy resins, mainly due to the development of certain application fields including adhesives, composites and electronics [9,12].

Adhesives based on epoxy resins have outstanding strength properties due to the powerful bonds that can be formed between similar and dissimilar materials such as metals, glass, ceramics, wood, cloth, and many types of plastics. In fact, the cohesive strength of a properly cured resin is also very high so that sometimes failure under stress occurs within the material being bonded rather than within the glue line itself.

The variations in epoxy formulation ensure that a range of adhesives of very wide versatility can be prepared. This has allowed the applications for epoxy resin adhesives to develop from their original use of metal bonding in the aircraft industry to widely differing industries.

In applications for building, one of the first structures where precast concrete units (slender cruciform columns) were bonded with an epoxy adhesive system was at Coventry Cathedral, Britain, 1960-1962 [13]. Other early examples include the Sydney Opera House (shell roof), 1963-1967 [13], the Sygar Terminal in Durban (precast concrete arches), 1965[14], and the Olympic Stadium (console cantilever arm and anchoring 'banana' beam) and the Velodrome roof (Y-shaped ribs) constructed for 1976 Olympic Games in Montreal [15].

In bridge construction, this technique has been successfully used since 1962 in many parts of the world including North America [13,16,17]. It is practicable and reduces construction time and overall cost.

Reinforcing of structures through epoxy-bonding of steel plates to concrete beams dates back to the mid 1960's. Between 1965 and 1967, three buildings in South Africa were strengthened using this technique[14], while laboratory tests in France were carried out on simply supported beams reinforced by steel plates from beneath[18]. Since then, this technique has been widely used in the strengthening of existing buildings and road bridges using steel plates, beams and angles [13,15,16,17]. Another example of composite construction pioneered in South Africa in the early 1960's was the epoxy-gluing of brick panels into the reinforced concrete frames of the building [14]. This enhanced the strength at an economical overall cost.

Epoxy adhesive systems are extensively used in concrete-concrete and metal-concrete bonding due to their excellent adhesion characteristics [13,17,19,20]. Such systems also perform well in bonding glass to ceramics. An early example is the lantern of the Cathedral of Christ the King, Liverpool, 1968, where glass-concrete panels are bonded with an epoxy adhesive [13]. Prefabricated panels with stone veneers, brickslips, metal and ceramic tiles, and wood as well as certain plastic laminates bonded to concrete backing with epoxy adhesives are common in buildings today [19,21]. These adhesives are also used for bonding exterior claddings and interior finishes to brick, concrete and concrete-block walls [19,21]. Building surfaces are at times finished through setting stone aggregates in an epoxy mastic [20]. Also certain facade panels consist of a rigid plastic insulating core sandwich between epoxy mortar panels [16].

In addition, epoxy adhesives are used in polymer concrete and in mortars for industrial and heavy-traffic flooring, floor coating compounds and the bonding of most floor tiles [8,16,19,21]. Epoxy adhesives are extensively used in crack injection for structural repairs of bridges, roads, tunnels, dams and historic stone and brick structures. Other uses include grouting foundations for heavy machine installation, pile bonding and clay-pipe bonding [15,22]. Epoxy adhesives are sometimes used for resilient floor coverings where high strength and water resistance are required [21]. They are also used in bonding rubber and some plastics to ceramic, and certain ceiling finishes such as glassfiber mat panels [19,21]. Epoxy adhesives have also been successfully utilized in stone consolidation and preservation.

The adhesives are most commonly used as two-component fluids or pastes, which cure at room or elevated temperatures. Some adhesives are supplied in rolls as a supported sheet, i.e., a glass fabric tape impregnated with adhesive, which is simply called a tape. Polyethylene on both sides of the tape keeps it from sticking to itself in the roll. Just before use, the polyethylene is stripped off and discarded. Other forms of the adhesive are powders, pellets or rods. The tapes and various forms of solid adhesive contain both resin and a curing agent component. There are also pastes that contain both components. In all of these cases the adhesive is ready for use. Nothing further needs to be added and no mixing is required. The curing agent used is latent and only begins to react with the epoxy resin at elevated temperatures. Hence the one-component types all require heat for curing.

There are, of course, some limitations to the use of epoxy resin adhesives. Some materials such as certain crystalline or less polar polymers (e.g.,polyethylene, silicones, and fluorocarbons) do not bond effectively with epoxy. Careful surface preparation of the substrate is essential to realize the full potential strength of the adhesives.

The advantages of epoxy resin adhesives may be summarized as follows [23-30]:

i. Their versatility in bonding a wide range of materials with flexible or rigid bonds, which retain their strengths from -50°C to +300°C.

ii. The extremely high bond strengths can be achieved.

iii. Low temperature curing is possible, accompanied by low pressure, often only contact pressure.

iv. No volatile solvent is present and nothing is vaporized during cure, which allows impervious surfaces to be bonded.

v. Very small shrinkage occurs during cure, and hence less strain is built into the glue line.

vi. The bonds formed show only low creep under prolonged stress and have good resistance to corrosion and many chemicals.

vii. Very good electrical properties. Typical formulations have the insulating resistivity of 10^{12} ohm-cm at 150°C or conductivity of 10^{-3} ohm-cm at 25°C.

1.4 LIGNIN AND LIGNIN DERIVATIVES

Lignin is a renewable, non-toxic, commercially available and low cost resource which has the potential of being utilized as a basic component for polymeric building materials [31-49].

Lignin is an important component of the plant kingdom. In chemical terms, lignin is a polymer consisting of both aromatic and aliphatic portions. Lignin has a heterogeneous branched network of phenylpropane units. Electron microscopy reveals that lignin is an amorphous compound which is deposited, along with the hemicelluloses. The phenylpropane units are held together in many ways by ether and C-C bonds (see Fig.1-4). Lignin is thermoplastic and has a glass transition temperature which may range between 127-193°C depending upon its molecular weight.

Lignin exists in a wide range of molecular weights. The

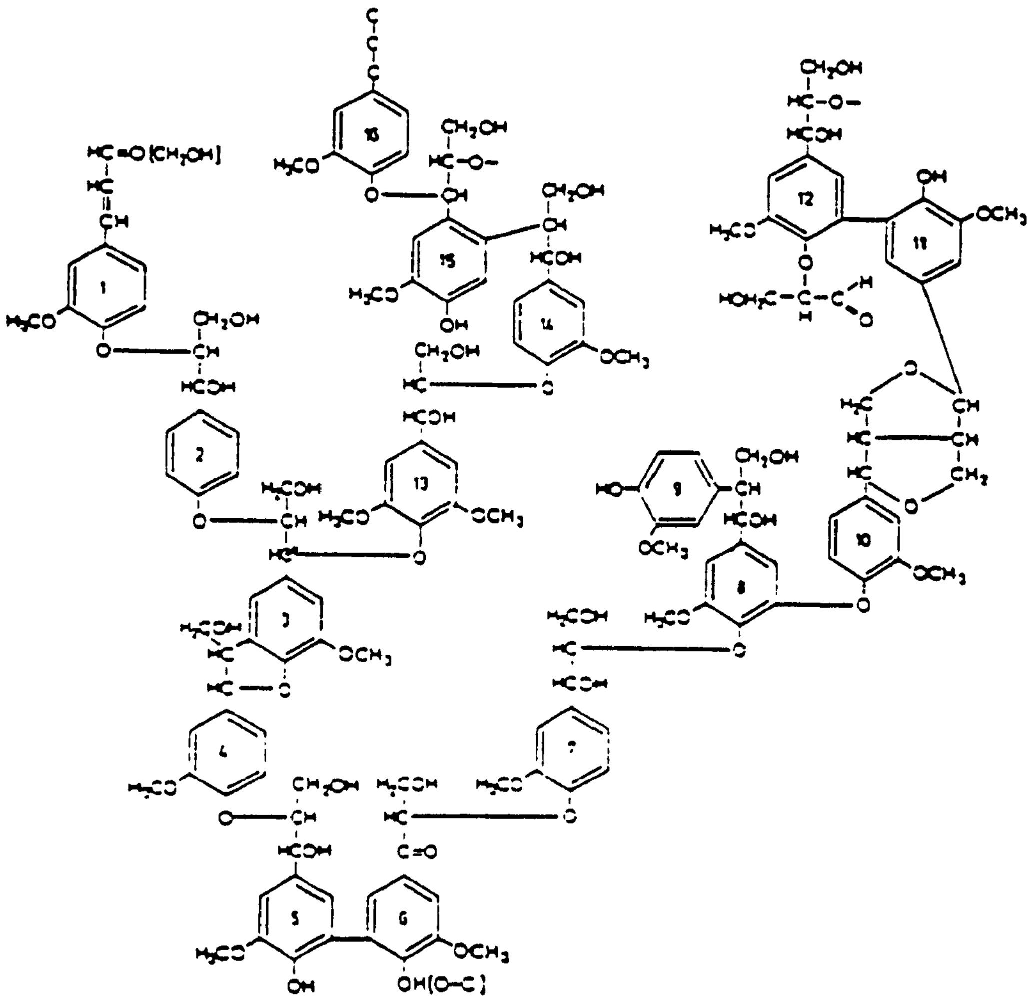


FIG.1.4 BASIC STRUCTURE IN SOFT WOOD LIGNIN
SHOWN WITH 16 PHENYL PROPANE UNITE [32]

molecular weight (Mw) for isolated lignins is in the range of 1000 to 12,000, depending upon the extent of degradation and condensation during isolation.

Plant lignins can be divided into three broad classes, which are commonly called softwood (gymnosperm), hardwood (dicotyledonous angiosperm), and grass or annual plant (monocotyledonous angiosperm) lignins.

In plants, cellulose fibres are bonded to lignin. There are two main methods for making chemical pulp (i.e. isolating cellulosic fibres by chemical means which consists mainly in removing the lignin from wood or other plant material to release the fibres):

i. the acid sulphite method, and

ii. the alkaline kraft pulping methods.

In the acid sulphite method, wood is cooked with salts of sulphurous acid whereas in the alkaline kraft process, it is cooked with a solution (white liquor) containing sodium hydroxide and sodium sulphide. The dark solution of the degraded lignin dissolved out of the wood is called spent sulphite liquor in the sulphite process and black liquor in the kraft process. In the alkaline kraft process the black liquor is concentrated and used as a fuel. This approach also recovers the alkali needed to prepare the cooking liquor and furnishes the heat, steam and electric power necessary for the industrial process.

The most significant and urgent problem is the profitable utilization of the vast quantities of lignin available as waste products or byproducts of the forest-using industries and, especially, the pulp and paper industry.

For more than three quarters of a century the chemical pulping industry has been utilizing essentially only half the tree as pulp, and has been discarding the other half as a waste or as a source of heat. Pressures for the abatement of pollutional effluents, the need for conservation to meet expanding requirements for our raw materials, and the urge for more economical production in the face of higher operating costs have been responsible for initiating research on the utilization of the other half of the tree.

Before World War II, the pollution abatement incentive was the motivating factor in most research in this field, but since that time the other two factors have been responsible for more and more of the research in byproduct utilization in the pulp industry.

1.5 POLYBLENDING

Since the early 1970's, there has been an increasing concern with the future supply of energy and materials. The cost of most materials, including synthetic polymers, usually rises with rising energy costs [50].

Polyblending has become one of the most commercially important and inexpensive ways to develop new materials from readily available base polymers [51-58]. The main aim of polyblending is the production of high-performance materials at a reduced cost. This is achieved through an infinite number of blending possibilities, the ability to use existing or more flexible processing equipment, and the capacity to combine expensive polymers with inexpensive and abundant ones.

Polyblending is the physical blending of two or more polymers. The usefulness of polymers can be considerably increased by polyblending carefully selected polymers in appropriate proportions, such that the end product has more desirable properties than those of its components. The combining of two or more structurally dissimilar polymers is of commercial interest due to the potential of developing materials to meet specific functional needs in industry. Curing time, durability, mechanical performance, or other properties may be altered to suit industrial requirements; cost reductions are possible through suitable selection of materials without sacrificing the inherent properties of the functional polymer.

Blending two polymers usually leads to a class of materials whose properties are due to the presence of two components. The occurrence of synergistic effects may yield superior properties within the polyblend compared to those of either component.

The properties of polymers are changed by polyblending because the macromolecular environment of the polymeric matrix is modified; bond energies and chain flexibility between molecular groups and blocks are altered due to adhesion and interaction between distinct polymeric phases. Hence, phase morphology is an important consideration in polymer blend technology since they critically influence many properties and subsequent uses of the end products.

Polyblends are immiscible (incompatible, heterogeneous) or miscible (compatible, homogeneous). Due to the inherent incompatibility of different polymer chains, polyblends do not usually form true solid solutions. When two distinct phases remain upon mixing, the polyblend is considered immiscible. In miscible blends, due to mutual solubility, a mono-phase system is formed.

Apart from the properties of the constituent polymers, the properties of polyblends depend upon the morphology of the blend. The size, shape, distribution and degree of separation of the dispersed and continuous phases will in turn depend upon the following:

[1] Interfacial adhesion properties of the polymers.
[2] Volume ratio of the components.
[3] Interaction of constituent polymers.
[4] Molecular weight and structure of each polymer.
[5] Blending conditions including temperature and pressure.
[6] Method of blend preparation i.e. mixing, open-rolls blending, extrusion and so on.

In general, miscible polyblends exhibit optical clarity, a single sharp glass transition temperature, and homogeneity at a submicroscopic level (50-100 Angstroms). The mechanical properties of such blends are usually superior to those of immiscible ones. Immiscible polyblends are usually opaque and have two Tg's which belong to each component and show true two-phasic behaviour.

CHAPTER 2

LITERATURE SURVEY OF POLYMER-LIGNIN SYSTEMS

2.1 DEVELOPMENT OF POLYMER-LIGNIN BUILDING MATERIALS

2.1.1 ENGINEERING PLASTICS

The potential use of lignin for the production of plastics has been established by a number of researchers in past years [42, 59-70].

Kratzl et al. [66] have investigated the reaction of lignin with phenol and isocyanates. These preliminary studies were designed to determine the potential utilization of lignin in the plastics industry.

Glasser et al.[59-66,68-72] have focused particularly on the possible use of lignin as a component in engineering plastics. Lignin designed as a high-impact-strength, thermally resistant thermoset polymer. It thus inherently has properties similar to those sought in some uses of engineering plastics. Central to this research effort was the chemical modification of lignin by hydroxyalkylation - forming hydroxypropyl lignin derivatives - to improve their viscoelastic properties as prepolymers for thermoset engineering plastics.

A considerable amount of data has accumulated regarding the modification of lignins to engineering plastics [73]. Unfortunately, the incorporation of various monomers and polymers, such as di- and polyvalent epoxyphenols, esters and isocyanates, in the lignin structure in most cases resulted in brittle or tarry materials whose properties designated them as potential adhesives, lacquers, dispersants and films, but not as structural materials [74,75].

Recent systematic study on the relation between network structure and substituent in kraft lignin or steam exploded lignin have shown that the lignin containing networks can be modified in new ways [65,76]. The toughening of glassy, structural thermoset can be achieved by incorporating a variety of polyether and rubber-type soft segment components in the polymer network structure.

Glasser and co-workers [77] applied this principle to lignins. They found that toughening elements can also be built into these materials to form elastic polyurethanes through hydroxyl functionality, acrylate from vinyl functionality, and epoxy from amine functionality. Also Kringstad and co-workers have been working on similar research projects [78].

According to Glasser [79], the relatively low glass transition temperature and the decrease in brittleness can be explained by introduction of soft molecular segments capable of a plastic response to mechanical deformation. The introduction of hydrophilic polyether segments which results predominantly in single phase morphology, and less polar rubber segments seems to favour two-phase morphology.

The use of lignin in polymer blends, e.g., with polyvinyl alcohol [80] with no sign of phase separation, is a new promising technique. It is found that blends prepared by injection moulding have consistently better material properties than blends prepared by usual solution casting.

Glasser et al. are also studying several other lignin-based polymers [71]. For example, the examining structure-property relationships of soft segment-containing lignin-based polyurethanes. They prepared hydroxypropyl lignin-based thermosetting polyurethane containing polybutadiene glycol or polyethylene glycol soft segments, crosslinked with diisocyanates. They find that introduction of the soft segments significantly influences the mechanical and thermal properties of the polyurethanes.

The above methods of incorporation of modified lignin in polymer networks and blends open new promising possibilities for the technical use of lignins and makes it competitive with other raw materials for engineering plastics.

2.1.2 ADHESIVES

Various attempts have been made to prepare lignin based adhesives [81-108].

Most adhesives in their physical form, or when applied, are required to be highly viscous liquids so as to have good spreadability and ease of application. Waste liquor from pulp industries is also found to have a relatively high viscosity and a sticky nature. Hence, from its very appearance, waste liquor may give the impression that it could also be applied as an adhesive. Lignin, the major constituent of waste liquor, is a natural binder in wood and is one of main constituents imparting mechanical strength to wood.

A pressure sensitive tape [109] with high storage life results when the concentrated waste liquor of the sulphite process is treated with 1% of phosphoric acid, then blended with about 10% poly(vinyl alcohol) and finally with urea or thiourea (10-25%). The quality of the product can be further improved by adding a sulphur dioxide releasing compound. Water soluble gummed adhesive tape [110] can be made from the lignocellulosic material by hydrolysing it under high temperature and pressure followed by extraction with a solvent like methanol or acetone. On drying, a satisfactory product is obtained. Sodium lignosulphonate from sulphate waste liquor is heated with formaldehyde in the presence of an NaOH solution and heated with phenol for 20-60 min at 80-110°C [111]. This copolymer is used in the preparation of particle board, hardboard, plywood, etc.

An adhesive based on lignosulphonate has been made for use as binder in ceramic/tile/concrete formulations [112]. A typical recipe for binder for ceramics is as follow: lignosulphonate 10; $CaSO_4.5H_2O$, 10-12; kaolin, 8-10; $Na_2Cr_2O_7$, 2-2.2; and glycerol, 3-4 parts [112].

Glasser and his co-workers [69] have synthesized a lignin adhesive with isocyanate and melamine. Hydroxyalkylates kraft, organosolv, steam exploded and H_2SO_4 lignin samples were formulated with crosslinking agents (i.e. polymethylene-polyphenylene-isocyanate and hexakis(methoxymethyl)melamine) and used as wood adhesives in emulsion and solvent-based systems. Shear block tests indicated that strength properties of adhesives decline on average by 15%, as compared to polymethylene-polyphenylene-isocyanate, with the contents of lignin derivatives in solvent-based formulations, whereas in emulsified formulations, adhesive performance was related to component solubility and compatibility. None of lignin derivatives containing adhesives had significant wet strength in 4 or 24 hours boil test.

The use of byproduct lignin in adhesives for wood composite products has been thoroughly reviewed by Forintek [113]. Tests have shown that a lignin-based adhesive developed by Iotech worked effectively in waferboard, although the required pressing time was longer than for traditional composites using phenolic resins.

L. Zhao et al.[114] have prepared some new wood adhesive derived from lignin. The practical application of the adhesive was studied in relation to the type of lignin and curing method.

Lignin-phenol formaldehyde formulations have been used in the manufacture of particleboard, fibreboard, and plywood, as well as other adhesive and board products. The reason for the development of these new adhesives must also be seen from the point of view of lowering the overall cost of production, since lignin, in the form of spent sulfite liquor or kraft black liquor, is less costly than phenol formaldehyde [81].

Lignosulphonic acid from spent sulphite liquor [115] on polycondensation with phenol and formaldehyde is found to give an adhesive suitable for use in the manufacture of fibre boards. When the lignosulphonate adhesive is modified with nitrobenzene, the resulting product has a high flexural strength. Particle boards in three plys were made from wood chip-bark mixture using 3-10% phenol-formaldehyde copolymer and 10% lignosulphonate-based phenolic resin pressed at 145-150°C for 10-15 minutes under a pressure of 17.5-21.0 kg/cm^2.

A two-step process [116] for the condensation of lignin gives a good binder for particle boards. The first step involves acid condensation with a small quantity of formaldehyde with phenol and sulphite liquor at 80°C(pH=4.0). The second step is alkaline condensation in the presence of some more formaldehyde.

In a process for making plywood, the conventional phenol-formaldehyde adhesive is replaced by phenol-lignin-formaldehyde copolymer prepared using lignin obtained from black liquor. On treating black liquor with HCl, lignin precipitates out and after filtration and washing it can replace phenol in phenol-formaldehyde resin to the extent of 60% [116].

Calcium lignosulphonate-based spent liquor when reacted with epichlorohydrin or formaldehyde and phenol gives an adhesive for plywood [117]. Sodium-lignosulphonate from sulphite waste liquor gives a good adhesive for plywood when it is polycondensed with p-formaldehyde in the presence of phenol-formaldehyde solution (40%) [118].

The cohesive strength of plywood is reported to be quite high when it is made using phenol-formaldehyde thiolignin copolymer [119]. A copolymer based on sulphate lignin from black liquor and phenol-formaldehyde is used as a glue for making three-ply plywood from Douglas fir veneers [120].

The adhesives for plywood particle boards described above could also find use in preparing structures based on raw wood. One of these adhesives is a polyurethane modified lignin [121]. The reaction of lignosite or kraft lignin-maleic-anhydride copolymer with propylene oxide in the presence of $ZnCl_2$-ethylene glycol gives a polyol, which on reaction with isocyanate leads to a polyurethane with the requisite properties for use as an adhesive for wood and for impregnation of paper. Wood adhesive can also be made from lignocellulosic material of calcium and ammonium based sulphite liquor. The process involves spray drying followed by vacuum drying of the spent liquor, acidification of calcium-based liquor and fractionation of the ammonium based liquor. The final product is made by hot pressing.

Roffael et al.[85-88] demonstrated the applicability of using sodium and ammonium-based lignin spent sulfite liquor as a substitute for conventional phenolic adhesives.

Approximately 25 and 35% of phenolic resin may be substituted in 20-mm thick one-layer, and three-layer particleboard respectively, without significant decrease in the mechanical properties of the board. The strength of 20-mm thick one-layer particleboard, formulated with 9.1% and 6.75% phenol formaldehyde content, showed no less in strength, in tension or bending (for the board containing a lower phenol formaldehyde content), yet a net saving of 25% in phenol-formaldehyde may be realized if spent sulfite liquor is used as the adjustment resin [88]. The particleboard properties were dependent on the pH value of the spent sulfite liquor having an optimum value ranging between 7 and 10. Particleboard properties were also reported to be a function of the pressing conditions. The crosslinking of the lignin macromolecular units occurred via a Lederer-Manasse type reaction, with side chains being linked by a Tollens reaction.

Adams and Schoenherr [92] were able to produce a high solids amount (40%) low viscosity lignin solution by dissolving kraft lignin in phenol-formaldehyde-alkali solutions. This copolymer, when compounded into a plywood adhesive used in the manufacture of three ply panels of Douglas fir, produced wood failures of 92% of the control.

Hollis and Schoenherr [122] used the same solution system in a two-step process to yield a resin having 37% solids content and 460 cP viscosity. The resin was formulated into an adhesive for use in plywood manufacture. Tests conducted on three-ply panels pressed at 140°C and 1.2 MPa for 6 min showed 94% wood failure of the control.

Forss et al.[123] used ultrafiltration to extract the high molecular weight fraction of alkali lignin to formulate a lignin-phenol formaldehyde adhesive suitable for use in the production of fibreboard, plywood and particleboard. In order to obtain a three-dimensional molecular network, less phenol formaldehyde is required to crosslink the high molecular weight in comparison to the low molecular weight fraction of alkali lignin. The reactivity of the low molecular weight fraction and its contribution to the formation of network linkages as well as the concentration of inorganic salts was not discussed, however their significance, as noted by others [81,91] cannot be overlooked. Tests on three-layer plywood, using 40-70% lignin content as adhesive, show that board properties are similar to those adhered with conventional phenol formaldehyde adhesives.

The patent [97] of Shen et al. was exploited commercially in Canada [96-98,124]. 6 and 13-mm waferboards are being produced at a resin cost of one-sixth that of commercial phenol formaldehyde resin. The results of test performed on waferboard produced with an equal amount of ultrafiltrated spent sulfite liquor and phenol formaldehyde clearly indicate that the mechanical properties of the product more than meet the minimum standards.

Calve et al.[99,100] have developed a relatively new formulation of ammonium - spent sulfite liquor adhesive resin, copolymerized with 30-40% liquid phenol-formaldehyde. Ammonium - spent sulfite liquor - phenol formaldehyde is of interest because it yields particleboard of exterior quality, practically free of formaldehyde emission. This adhesive, however, is more demanding compared to urea formaldehyde resin because it requires longer pressing times at higher temperatures.

2.1.3 FOAMS AND OTHERS

Moorer et al. [74] employed lignin in the formation of polyurethane foams, by dissolving lignin in glycol and then reacting it with diisocyanate. The reaction was described in terms of the isocyanate acting as a crosslinking agent, linking the two kinds of polyol. The hydroxyl groups in lignin were assumed to be the key to this reaction.

Kratzl and co-workers [66] sought to increase the number of reactive positions in lignin by condensation with ethylene oxide, propylene oxide, and an alkyl sulfide. The reactions were shown to produce hydroxyl groups suitable for mixing and reacting with diisocyanates in the formation of rigid polyurethane foam.

Low density polyurethane foams with acceptable strength and excellent flammability properties were formulated by Glasser et al with a commercial furan polyol containing 20% hydroxypropyl lignin [125]. Propylene oxide-modified lignin from two sources, kraft and organosolv lignin, were employed. The organosolv lignin derivative exhibited better forming characteristics than the corresponding kraft lignin, which collapsed when the rising foam was touched for testing. The weight contribution of lignin derivative was limited to 20% by compatibility with the fluorocarbon blowing agent, and solubility in polyol. Preliminary tests encourage further research on structural materials containing hydroxypropyl lignin derivatives.

The same team [70] has undertaken a series of studies related to the formation of polyurethane films prepared from chain-extended hydroxypropyl lignin (CEHPL). The thermal, mechanical, and network properties of these PU's were investigated by DMA and DSC analysis. All films exhibited single glass transition (Tg) which varied between -53° and $101^{\circ}C$, depending on lignin content. From swelling experiments, molecular weight between crosslinks was determined and found to vary over 2.5 orders of magnitude. These values were related to the change in Tg that accompanied network formation. Stress-strain experiments showed a variation in Young's modulus between 7 and 1300 MPa. Most of the variation in material properties was related to lignin content and to a lesser extent to diisocyanate type (i.e. hexamethylene diisocyanate or toluene diisocyanate). The source of the CEHPL had no effect on the properties of the polyurethane and these products can be controlled and engineered for a wide variety of practical uses.

Lignins from various sources are employed as in the formulation of polyurethane network films [67]. The lignins included a milled wood lignin (red oak), a kraft lignin, an organosolv lignin, a steam explosion lignin and an acid hydrolysis lignin. The network like materials are evaluated by DSC, DMA and swelling. On the basis of the results a classification method of lignin prepolymers for use in (polyurethane) network like materials is advanced, which is based on the rise of the Tg, as a result of crosslinking. This rise in Tg can be expressed as average molecular weight between crosslinks, using relationships proposed previously. Agreement between experimental (based on rise of Tg) and theoretical (based on synthesis parameters and stoichiometry) data suggests good network forming qualifications of a prepolymer, and disagreement indicates the formation of a non-uniform network with a large fraction of soluble material. The hydroxypropyl derivatives were comparable to the corresponding hydroxypropyl lignins, which in turn outperformed the parent lignins. Lignins ranked in the order of increasing qualifications for network formation as follows: acid hydrolysis, milled wood, kraft, organosolv and steam exploded lignin. The results suggest that solubility is the key parameter determining uniformity and structural material properties of the lignin prepolymers in thermosetting networks.

2.2 FUNDAMENTAL ASPECTS OF POLYMER-LIGNIN SYSTEMS

Chodak et al [126] investigated the influence of lignin addition on the crosslinking characteristics of polypropylene (PP). In order to demonstrate the effect of various lignin functional groups on the properties of PP, kraft lignin and several of its derivatives were investigated as potential additives. The results show that polymerization of polyolefins are influenced mainly by hydroxyl (OH) groups present in the lignin. Unmodified kraft lignin has the greatest effect on the radical transformation reaction, since it contains many more OH groups than the lignin derived additives. It was also observed that the reactivity of aromatic OH groups (i.e. those attached to the aromatic ring in lignin) was greater than those of the aliphatic OH groups.

Klason and Kubat [127] have used lignin as a filler in high density polyethylene (HDPE) and PP. Lignin appears to behave as a reinforcing filler which , when combined with either HDPE or PP, serves to moderately increase the modulus of these polyolefins. These results were satisfactorily predicted using the Halpin-Tsai equation as modified by Niesen.

Kratzl et al [66] investigated the reaction of lignin with phenol and isocyanates . These preliminary studies, designed to determine the potential utilization of lignin in the plastics industry, showed that in the case of lignin-isocyanate reactions, few products of technical value could be obtained. This was due to the scarcity of active positions within the lignin macromolecular structure. Much of the work related to polymer-lignin products has since focused on increasing the reactivity of the lignin by modifying specific reactive groups to enhance the polycondensation process.

Glasser at al [59-62,71,72,128-132] have conducted a study to elucidate the mode of formation of new polyurethanes synthesized from lignin isocyanate combinations. They demonstrated that lignin may be carboxylated by reacting it with maleic anhydride to form a nonhydrolyzable copolymer. The carboxyl and phenolic groups of this copolymer offer reactive sites for oxyalkylation to a polyol. This may be achieved by reacting the saponified copolymer with propylene oxide in the presence of an alkali catalyst. The carboxyl groups are esterified, and the phenolic and aliphatic hydroxyl groups are etherified to yield a highly viscous, homogeneous active and polyfunctional polyester-polyether polyol suitable for mixing and for reaction with diisocyanates. To further demonstrate the versatility of lignin as a coreactant in polyurethane formation, Glasser et al [130] undertook the production of polyurethane foams from carboxylated lignin.

The structure of any thermosetting resin can be described in terms of a relatively high molecular weight backbone polymer that is tied together by crosslinking segments. The properties of the network are then determined by the nature of the two components (main polymer and crosslinking agent) and the number of crosslinking sites introduced into the system (crosslinking density). By changing any one, or any combination of these structural features, the properties of the network are changed, allowing for the formulation of products with a wide range of properties. Based on this premise, Glasser et al [59-62,131,132] conducted a series of tests on hydroxypropyl lignin polyol-isocyanate derivatives. They established the effect of the crosslink density on polyurethane films properties by varying both the NCO/OH stoichiometry and the hydroxyl content of hyroxypropyl-lignin polyol. The maximum effective crosslinking was found to occur at a NCO/OH ratio of 3, after which the density levelled off. It is suggested that the higher concentration of diisocyanate, in comparison to conventional polyurethane systems (i.e. 3:1 vs 2:1), is due to the high polydispersity of the lignin polyol, which excludes incorporation of lower molecular weight fractions into the network. Thus the influence of the sol fraction on the physical properties of the polymer network was significant, but the manner and the degree to which it affected the overall behaviour of the network could not yet be ascertained. The crosslink density was found to vary directly with the hydroxyl content of the polyol. The Tg of the polyurethane films varied linearly with the crosslink density of the network. The dynamic mechanical properties of the films were found to be sensitive to the weight fraction of extractable part in the network.

Saraf et al [71] studied polyurethane synthesized from blends of hydroxypropyl-lignin (HPL) derivatives with polyethylene glycol (PEG). The effect of soft segment incorporation in relation to content and molecular weight was examined on the basis of thermal and mechanical properties. A steady drop in Tg was observed, with increasing PEG (soft segment) content and a significant increase in Tg with rising molecular weights. The tensile behaviour was considerably modified by the addition of even minor percentages of PEG. Both Young's modulus and tensile strength decreased with increased PEG content, whereas the ultimate strain at break increased for similar percentages of PEG in the blend. Hence the mechanical properties were particularly sensitive to glycol content. Uniformity in structure, reduction in brittleness, and considerable improvement in mechanical properties with the inclusion of minor PEG constituents, indicated that the lignin-based network polyurethane could be synthesized with a wide range of performance characteristics. In a subsequent experimental program [72], the effect of concentration of polybutadiene glycol (PBDG) in a mixture of HPL was examined in relation to the thermal and mechanical properties. A phase separation between the two polymer components in the polyurethanes was detected by thermal and mechanical analysis. This effect was evident for nearly all degrees of mixing. It was concluded that polyurethane films behaved like rubber-toughened lignin networks when PBDG was the discrete phase, and like lignin-reinforced rubber when the lignin derivative phase was discrete.

Yoshida et al [133] found that at low NCO/OH ratios, kraft lignin contributed effectively to the formation of three- dimensional polymer network. When an optimum quantity of kraft lignin (5-20% depending on the NCO/OH ratio) is used, the resulting polyurethanes show improved mechanical properties compared to the polyurethanes synthesized with the polyether polyol as the only polyol component. At high contents of kraft lignin (> 30%) the polyurethanes were hard and brittle regardless of the NCO/OH ratio used. This is attributed to the combined effect of increased crosslink density and of an increase in chain stiffness.

Yoshihiro Sano and his coworkers [134] have investigated the utilization of lignin in resorcinol resins (RF). High molecular weight solvolysis lignin (B-CWL-1) and low molecular weight solvolysis lignin (B-CWL-2) were isolated in yields of 14.8 and 12.8%, respectively, from spent liquor which was prepared in the cooking of beechwood with cresols and water (7:3) including a small amount of acetic acid for 2 h at 170°C. The pulp was obtained with 7.3% Klason lignin. B-CWL-1 with MW 3500 (by GPC) and B-CWL-2 with less than 700 of MW. Three different approaches were tried in preparing lignin-based resorcinol resin adhesives. Adhesive-1 was a mixture of lignin-based phenol resin (LPF) and resorcinol. LPF was made by condensing B-CWL-1 and phenol (9:1) with HCHO. Adhesive-2 was a mixture of RF and an aqueous NaOH solution of B-CWL-1 or 2. RF was prepared by the usual method using resorcinol and HCHO. Adhesive-3 was a mixture of RF and lignin-based resin (LF). LF was prepared by reacting B-CWL-1 or 2 with HCHO. Paraformaldehyde and a filler were added to each of the adhesives for use in making 3-ply plywood panels. Adhesive-3 was the best of the lignin-based resorcinol resins. Tensile shear strength tests showed that as much as 80% of the resorcinol resins could be replaced by B-CWL-1, and also as much as 60% could be replaced by B-CWL-2. With adhesive-2 being more convenient, more than 60% of the resorcinol resins could be replaced by B-CWL-1.

Utilization in phenolic resins was also studied in terms of different solvolysis lignins. Hence, solvolysis lignins derived from oakwood and beechwood and isolated by solvolysis pulping using a cresol-water system, were studied in the context of their potential use as an extender or modifier of a phenolic based adhesive system. It was found that at least 90% of the phenolic resins can be replaced by each lignin. If necessary, each of the lignins can be condensed with HCHO in order to produce phenolic-type resins, and also the temperature of the hydraulic press for the preparation of the tested plywood can be lowered from 140 to 120°C.

L.P. Kovrizhnykh et al.[135] have studied a system based on urea resins with industrial lignosulfonates. Replacement of 20-30% HCHO-urea resin with Na or Ca lignosulfonate gave good-quality binder for particleboards. The binder cured rapidly in the presence of 2% $(NH_4)_2S_2O_8$. The obtained boards had good physico-chemical properties and a lower emission of HCHO than boards bonded with pure HCHO-urea resin.

In their another work [136], lignosulfonates treated with $(NH_4)_2S_2O_8$ were used in combination with urea resin as binders in the manufacture of particleboards. The curing of binder containing 30% lignosulfonates and 2% $(NH_4)_2S_2O_8$ was accompanied by a sharp decrease in free HCHO. The curing was a 2nd order reaction with reaction constant 0.083 L/mol-s for lignosulfonate-containing urea vs. 0.022 L/mol-s for unmodified urea resin. The particleboards based on urea resin-lignosulfonate binders exhibited high strength, good water resistance and low toxicity. The cost of particleboards was significantly by replacing 20-30% of urea with lignosulfonates.

It is also possible to modify lignin by grafting using, e.g., styrene or acrylic monomers. The grafting process is a free radical reaction which can be initiated either by radiation or by peroxide, as used in ordinary polymerization processes. Thus, acrylic monomers can be grafted onto lignosulfonates in aqueous solution using hydrogen peroxide/iron catalyst [137,138]. Experimental evidence has indicated that γ-radiation can also be used to graft styrene onto kraft lignin to give a product with similar solubility properties as polystyrene. The reaction seems to be promoted by methanol [139]. Also, acrylonitrile may be grafted by radiation to lignosulfonates with grafting yields of about 20%. However, the compatibility of the grafted product as a filler in SBR seems to be inferior to that of the original lignosulfonate[140].

Meister and Patil [141] have developed a method to chemically initiate free radical polymerization of 2-propenamide on kraft pine lignin with a molecular weight of 22000. Proof that lignin and poly(1-amindoethylene) are grafted together has been obtained from size exclusion chromatography, solubility, dialysis, and fractionation. The grafted lignin is an amorphous brown solid which can be crushed, and is insoluble in most organic solvents but does dissolve in water.

Poly(lignin-g-(1-amidoethylene)) and its hydrolysed derivative, poly(lignin-g-((1-amidoethylene)-co-(sodium 1-carboxylatoethylene))), exhibit a lower yield point, lower gel strength, and lower API (American Petroleum Institute) filtrate volume [141,142].

2.3 RESEARCH RELATED TO EP-L SYSTEMS

Epoxy resins based on lignin were reported by Mihailo et al. [143] in 1962. The lignin phenol resin was obtained by heating 100 parts lignin with 140 parts PhOH and 3 parts H_2SO_4 at 140-180°C, at which temperature phenol and H_2O distilled and the rest of PhOH was removed in vacuum to obtain the lignin phenol resin. Epichlorohydrin, methyl-ethyl-ketone and lignin phenol resin were mixed and 40% NaOH added during stirring and boiling. On the following day, the mixture was filtered and distilled, separating the epoxy resin.

Ball et al. [144] reported epoxy-lignin resins in 1962. A resin casing was produced by heating 50 grams of an epoxy intermediate of the diglycidyl ether of bisphenol to 190°C, and 17.5 grams of lignin was added and dissolved. The resulting solution was cooled to 120°C, and 33 grams of phthalic anhydride were added. The temperature was then raised to 130°C to assure dissolving of the phthalic anhydride in the lignin-epoxy solution. The solution was poured into molds which were heated to 160°C and kept at that temperature for 45 minutes, by which time an initial curing had occurred. The initially cured resin was removed from the molds after cooling and then subjected to a temperature of 136°C for 60 hours to attain a final curing.

Nabuo Shiraishi [145] has also made an attempt to prepare lignin-epoxy resin adhesives through a chemical way. However, in order to improve its reactivity, kraft lignin was first phenolated with bisphenol-A. For phenolation, a small amount of aqueous hydrochloric acid or BF_3 -ethyl etherate was used as catalyst. The phenolation with bisphenol-A was found to enhance the solubility of the lignin derivative. In fact, the lignin-epoxy resins obtained were found to be completely soluble in certain organic solvents, including acetone. The gluability of two types of epoxy-resins, prepared from lignins with different degrees of purity (Tokai Pulp kraft lignin F with less than 4.5% sugars and Oji kraft lignin with 11.7% sugars) were examined. The enhanced gluability was noted for the less purified lignin, suggesting active participation of the sugar components. Both epoxy resins gave satisfactory dry- and wet-bond strengths after 5 min of hot-pressing at 140°C. The gluability of the lignin-epoxy resin adhesives was found to be improved by the addition of calcium carbonate (50% by weight) to the liquid resin. This must be attributed to the nature of the weak alkali in calcium carbonate as a cure accelerator, and to the reinforcement effect of fillers. Besides hydrochloric acid, BF_3 is known to be an effective catalyst for the introduction of phenol groups into lignin. BF_3 is also known as a catalyst which can promote glycidylation not only of phenolic but also of alcoholic hydroxyl groups. Thus, the preparation of lignin-epoxy resins with BF_3 as catalyst was studied also. The epoxy value found for the standard lignin-epoxy prepared in the presence of BF_3 was 0.48, whereas that of the epoxy with HCl as catalyst was 0.38. The lignin-epoxy resins from the reaction in presence of BF_3 were also tested as adhesives for plywood, using triethylenetetramine as curing agent with hot-pressing at 140° C. The results of adhesion tests showed that water-proof adhesive strengths were improved by use of BF_3 as catalyst.

This permitted the adoption of hot-pressing times as short as 3 min for preparing three-ply plywood panels with 6 mm thickness. This resulted in satisfactory waterproof adhesive performance. The addition of calcium carbonate (50% by weight) to the liquid adhesive was again found to enhance the waterproof gluability.

An epoxy resin was synthesized on the basis of lignin by reaction of epichlorohydrin with hydroxypropyl lignin which has been reported by W.G. Glasser [146]. A mixture of a quaternary ammonium salt and potassium hydroxide was used as catalyst. Additional KOH was added stepwise at a rate which compensated for KOH consumption during dechlorohydrogenation. The epoxidation reaction was first studied using hydroxypropyl guaiacol as a lignin-like model compound. At room temperature, and when epichlorohydrin was in excess, the reaction was completed in five days. The reaction was found to be highly dependent on the stepwise addition of KOH, and it was independent of epichlorohydrin concentration. The maximum conversion of hydroxy to epoxy functionality was found to be 100% to 50% for model compound and lignin derivative, respectively. The lignin-epoxy resin was crosslinked with diethylenetriamine, amine terminated poly(butadiene-co-acrylonitrile) and phthalic anhydride. Sol fraction and swelling behaviour, and dynamic mechanical characteristics of the cured lignin-epoxy were studied in relation to cure conditions.

Tomita and his co-workers [147] reported the preparation of pre-reacted ozonized lignin/epoxy resins. Ozone has recently become industrially available at low cost. In the experiment, the lignin (50 g) was dissolved in a mixture of dioxane (500 ml) and methanol (1000 ml), and ozonized at 0°C with an oxygen flow rate of 0.5 ml/min and ozone concentration of 3%. After ozonization, the solution was treated with an excess amount of ether, and the insoluble fraction was filtered off, followed by drying under vacuum. The ozonized lignin was mixed by stirring with DGEBA and heated at 120°C. After heating for 30 min, the mixture was cooled to room temperature. The solidified reactants were dissolved in acetone (2ml) and the curing reagents, diethylenetriamine or hexamethylenediamine, were added at 90% of the stoichiometric amount to epoxy equivalent. Curing was generally done by heating at 130°C for 2 hours and allowing the product to stand at room temperature for one day.

CHAPTER 3

THE DEVELOPMENT OF EP-L POLYBLENDS AND THEIR ADHESIVE PROPERTIES

3.1 INTRODUCTION

On the basis of a literature survey (Chapter 2), it is known that researchers have made an attempt to prepare epoxy-lignin systems through chemical synthetic methods, which usually consist of high temperature chemical processes or catalytic reactions. Following such studies lignin utilization is possible but it requires important and costly chemical modification. These face a quality difficult control, because of lignin's natural variability, inhomogeneity and complex macromolecular structure. These may be some of the problems in the production of useful polymeric products from lignin.

In this study [2,4], as an alternative to chemical modification and chemical synthesis, lignin, as it results as a byproduct from different commercial processes, is directly used, without any modification, in a very simple and economical blending. That is, a liquid epoxy prepolymer and hardener or other additives are simply physically mixed with lignin at room temperature.

3.2 CHARACTERIZATION OF COMPONENTS

3.2.1 EPOXY

An epoxy adhesive system is primarily based on an epoxy prepolymer and a hardener. The epoxy prepolymer used in this study (Chapter 3,4,5) was a commercial 1200 CA resin , from Ciba-Geigy of Canada. Its main chemical component is diglycidyl ether of bisphenol A. The equivalent weight is 180 g/equiv. The crosslinking component, HY2992 hardener, is an aliphatic polyamine with an equivalent weight of 55 g/equiv.

Both the epoxy prepolymer and the hardener are liquids at room temperature. Their stoichiometric mixing ratio is 3.3:1.

This commercial structural adhesive can be used for the bonding of steel, aluminum, hardened concrete masonry and other materials. As an adhesive, it is recommended for applications to horizontal, vertical and overhead surfaces. Mixed with aggregate, 1200 CA forms a workable repair mortar.

3.2.2 LIGNIN

The second polymer, kraft lignin, is a commercial byproduct, referred to as Tomlinite and is produced by Domtar. It is precipitated from the black liquor of a mixture of hardwoods with sulphuric acid and its pH is adjusted to about 6-7.

The chemical and physical characteristics of lignin (brown powder) are shown in Table 3.1.

TABLE 3.1

CHEMICAL AND PHYSICAL CHARACTERISTICS OF TOMLINITE

Chemical Analysis:*

-C : 56.06%

-H : 6.03%

-S : 1.59%

-Total OH: 10.7%

-Methoxyl: 17.2%

-Carbonyl: 5.0%

Physical Characteristics:

-Specific gravity:** 1.28 g/cm^3

-Weight average molecular weight (Mw):*** 2800

-Number average molecular weight (Mn):*** 650

-Polydispersity (Mw/Mn):*** 4.3

---

* data furnished by Domtar Research Centre.

** determined according to ASTM D-153.

*** determined by GPC analysis on dried samples.

3.3 PREPARATION OF EP-L POLYBLENDS

The polyblends were prepared by manually stirring the epoxy prepolymer and a corresponding quantity of lignin (10-50% by weight) for two minutes at room temperature; the equivalent quantity of hardener was added and the mixture obtained was then stirred for another five minutes at the same temperature.

The initial low viscosity of the epoxy-hardener system facilitated dispersion of the lignin even in amounts up to 40%. When lignin was increased to 50%, the viscosity of the adhesive prevented a good workable mix from being made.

3.4 FACTORS WHICH INFLUENCE THE ADHESIVE JOINT SHEAR STRENGTH OF EP-L ADHESIVES

3.4.1 SHEAR STRENGTH TEST

By far the most common and useful type of adhesive test is the shear test. Not only it is quite simple and economical to conduct, but it of course also duplicates and evaluates the type of loading to which structural adhesives are most often subjected in service [148,149]. Shear stresses are produced by forces which act on the adhesive layer and which resist the movement of the adhesive in opposite directions [149].

The substrate material used in the adhesive joints was an aluminum alloy. The aluminum substrate surface was prepared by immersing it in a sulphuric acid-sodium dichromate solution at 60°C for 15 minutes, washing it with water to remove acidic traces and drying it at 100°C for 30 minutes.

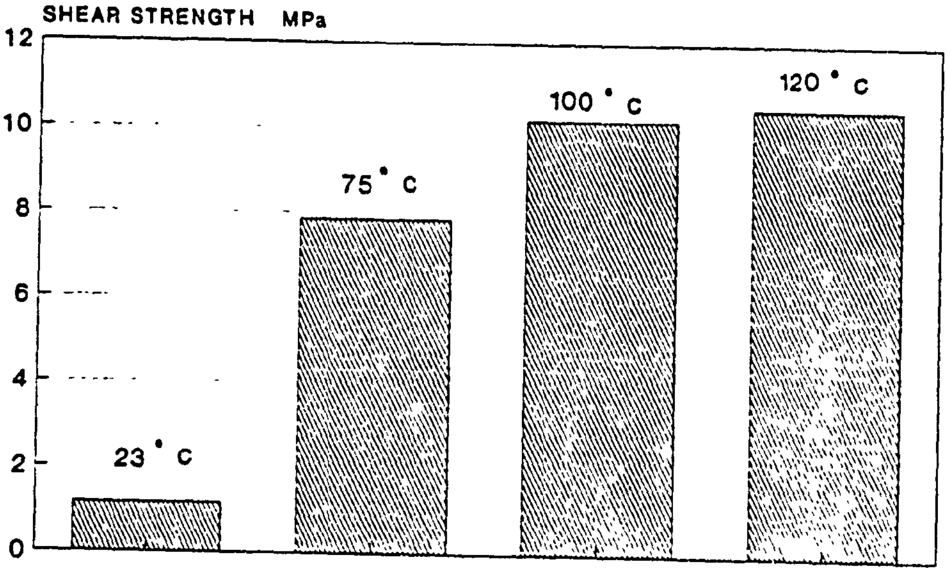
Single-lap shear joints with aluminum substrates (101.6x25.4x1.62 mm) were used for evaluating the adhesive shear strength by tension loading (ASTM D-1002) with an overlap length of 12.7 mm. The adhesives were applied across both sides of the overlap area. The adhesive film thickness was 0.22±0.03mm. During the cure, the specimens were under the constant pressure of 4 kg/cm^2. After curing for a certain time and at a certain temperature, these specimens were tested on an Instron model 1125 Universal Testing Machine at a crosshead speed of 2 mm/min, a chart drive of 20 mm/min and a testing temperature of 23°C. In all cases, values used for plotting results were averages of 5-10 determinations with the standard deviation of 0.01-2.37 MPa (see Appendix I). All the failure occurred at the adhesive/aluminum interface, that means it was an adhesive failure.

The factors which influence the adhesive shear strength are discussed as follows.

3.4.2 THE EFFECT OF CURING TEMPERATURE ON ADHESIVE JOINT SHEAR STRENGTH

The effect of curing temperature on the adhesive joint shear strength of EP-L40 is given in Fig.3.1 (curing time: 2 hours). It has been found that curing the blends at 75°C, slightly above the Tg of epoxy, had significantly improved their adhesive joint shear strength. When the curing temperature was higher than the Tg of epoxy, that is 100°C, even better results were obtained and there was not

Fig.3.1 EFFECT OF CURING TEMPERATURE
ON ADHESIVE JOINT SHEAR
STRENGTH OF EP-L40 [2]



EP:CA1200-HY2992
L:Tomlinite

much further increase at the 120°C curing temperature.

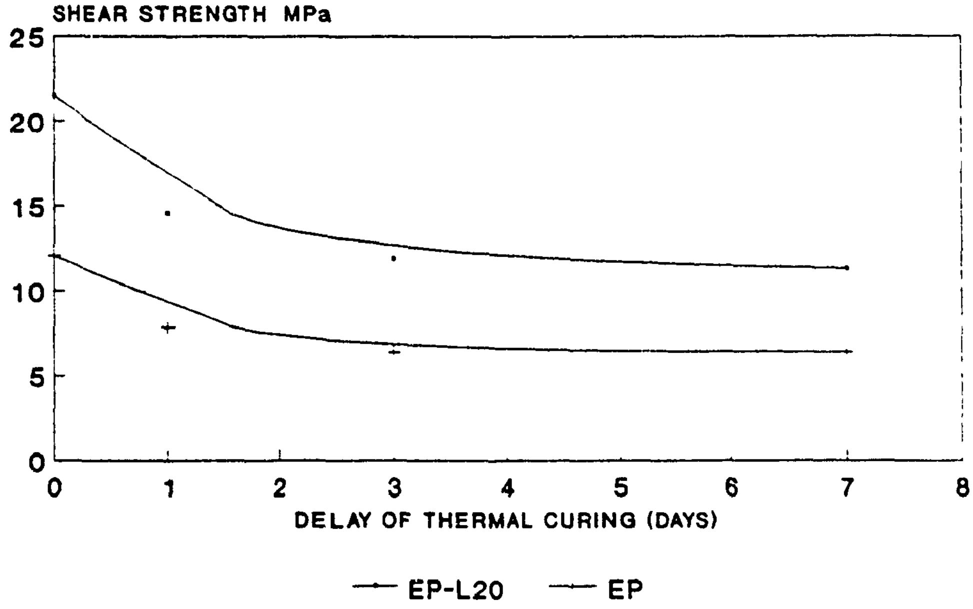
The shear strength of polyblend with 20% lignin obtained at 100°C curing temperature was about six times higher than that cured at room temperature. Curing at an elevated temperature (above Tg) increases the molecular thermal movement which allows more sterically hindered groups to interact and leads to greater crosslinking or interaction between components. This has the effect of improving the adhesive joint strength properties.

3.4.3 THE EFFECT OF CURING SCHEDULE ON THE ADHESIVE JOINT SHEAR STRENGTH

The sets of EP control and EP-L20 specimens were thermally cured (100°C, 2 h) following a scheduled delay of 1,3, and 7 days after their preparation. The results of the adhesive joint shear strength obtained in these conditions are shown in Fig.3.2. The storage of EP and EP-L20 samples at room temperature prior to the elevated temperature cure causes deterioration of the joint strength in both cases.

Fig.3.2 shows that the adhesive joint shear strength falls rapidly as the delay time increases up to 2 days, then falls slowly. This observation indicates an optimal curing schedule, i.e. specimens should be thermally cured immediately after their preparation if an optimal adhesive strength is to be obtained.

FIG.3.2 ADHESIVE JOINT SHEAR STRENGTH OF EP & EP-L20 vs. DELAYING OF THERMAL CURING [2]



EP:CA1200-HY2992
L: Tomlinite

3.4.4 THE EFFECT OF THE AMOUNT OF LIGNIN ON ADHESIVE JOINT SHEAR STRENGTH

The effect of the amount of lignin on the adhesive joint shear strength of the thermally cured polyblends is shown in Fig.3.3. The results are summarized as follows:

[1] Polyblends with 10%, 20%, 25%, and 30% lignin showed a considerable improvement in adhesive joint shear strength in comparison with the control EP (i.e. 53%, 78%, 39%, and 23% higher, respectively).

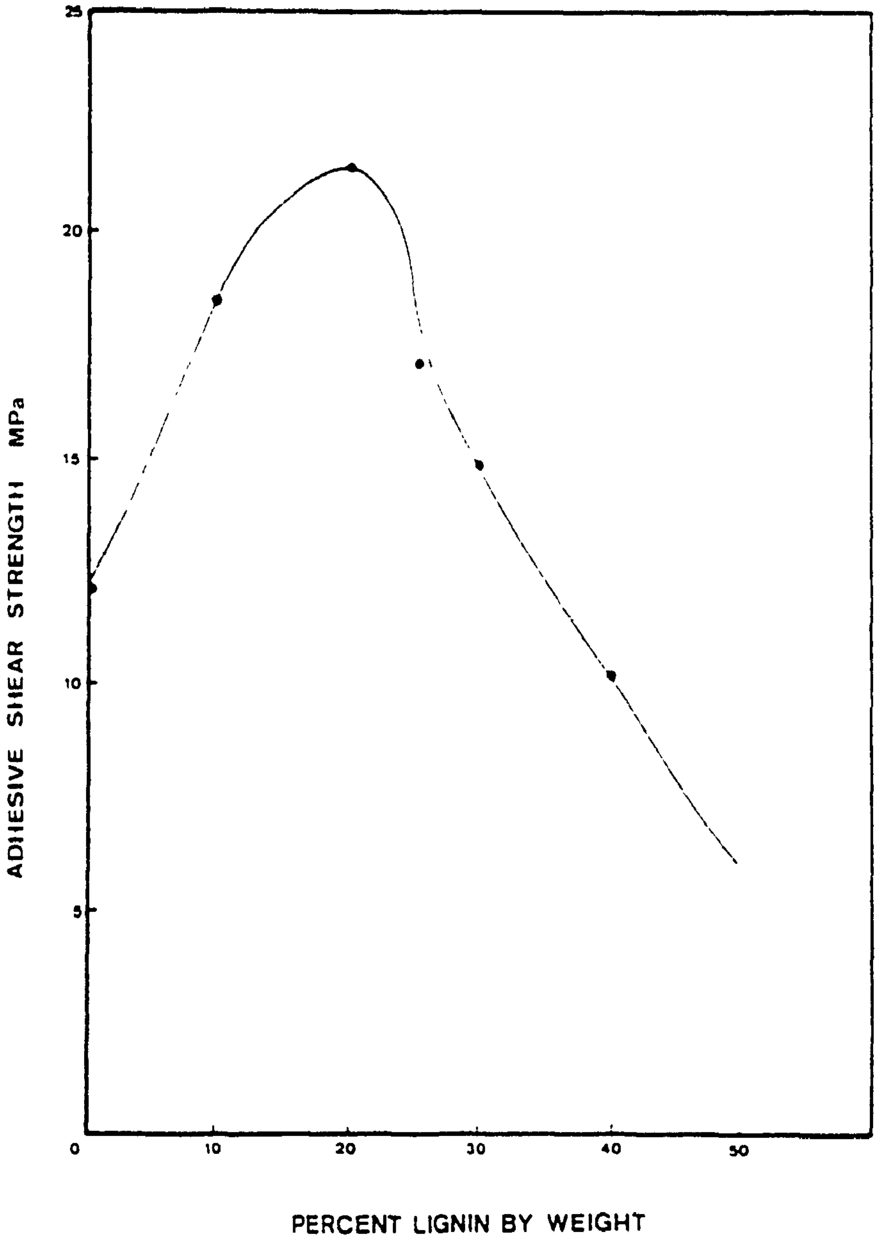
[2] The highest adhesive shear strength occurred at 20% lignin content, which is 178% of that of the control EP.

[3] For EP-L40 the adhesive shear strength was 16% lower in comparison with that of the control EP.

3.5 ECONOMIC EVALUATION

As we know, kraft lignin is a waste and byproduct of the pulp and paper industry. The utilization of lignin has significance for abatement of pollution. In the meantime, a significant benefit in terms of the cost of the new adhesive results, because kraft lignin is a very inexpensive commercial byproduct, and the blending process in this study is a very economical one. As shown in Table 3.2 and Fig.3.4 the cost of polyblends has been decreased to 90%, 81%, 76% and 71% of that of the control EP, while the shear strength has been increased to 153%, 178%, 139% and 123% of that of the control EP for EP-L10, EP-L20, EP-L25 and EP-L30 respectively.

FIG.3.3 EFFECT OF THE AMOUNT OF LIGNIN ON ADHESIVE JOINT SHEAR STRENGTH OF EP-L [2]



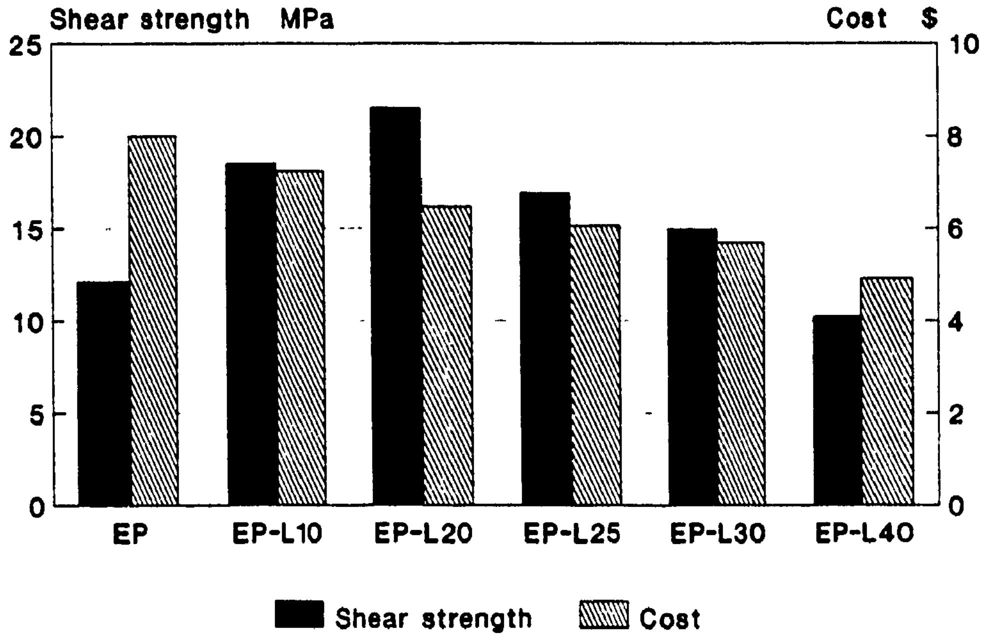
EP:CA1200-HY2992
L :Tomlinite

Table 3.2
Comparison of the Adhesive Joint Shear Strength & Related Costs of EP-L Polyblends

	Joint Shear Strength		Cost($)	Cost(%)
	MPa	%		
EP	12.1	100%	8.00	100%
EP-L10	18.5	153%	7.23	90%
EP-L20	21.5	178%	6.46	81%
EP-L25	16.9	139%	6.06	76%
EP-L30	14.9	123%	5.69	71%
EP-L40	10.2	84%	4.92	62%

EP: CA1200-HY2992
L: Tomlinite

FIG.3.4 ADHESIVE JOINT SHEAR STRENGTH AND RELATED COST OF EP-L AND THE CONTROL EP [6]



EP:CA1200-HY2992
L :Tomlinite

3.6 SUMMARY

In this chapter, the raw materials, i.e. epoxy and Kraft lignin, have been characterized. Some important parameters which influence the adhesive joint shear strength of EP-L adhesives have been established:

[i] The adhesive joint shear strength of EP-L increases as the curing temperature increases. An elevated curing temperature above the Tg of epoxy leads to a significant improvement in adhesive properties. The adhesive joint shear strength of EP-L20 cured at 100°C is about six times higher than that cured at room temperature.

[ii] The adhesive joint shear strength of EP-L increases as the amount of lignin increases with an optimal amount of 20%.

Based on these studies, the new EP-L adhesives have been successfully developed by an economical blending technique. These EP-L adhesives exhibit considerably improved adhesive properties and lower cost in comparison with the commercial epoxy adhesive. For example, the adhesive joint shear strength of EP-L20 adhesive is 178% of the control epoxy while the cost is 81% of the commercial epoxy.

CHAPTER 4

MISCIBILITY

4.1 INTRODUCTION

Why is lignin additive able to improve the adhesive joint shear strength of EP-L polyblends?

How does lignin additive improve the adhesive joint shear strength of EP-L polyblends?

To answer these questions, the following observations from Chapter 3 will first be discussed:

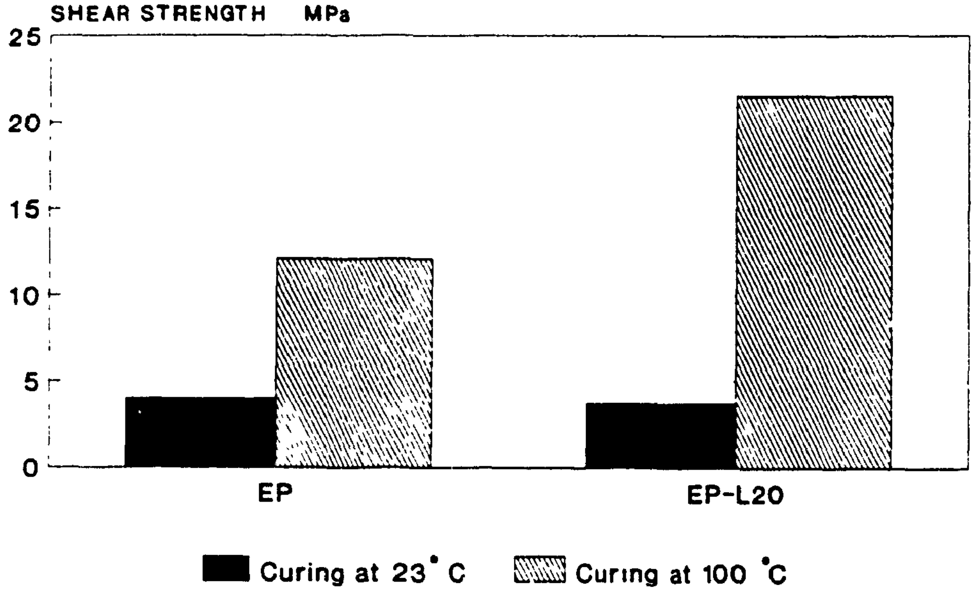
[a] As shown in Fig.4.1, the adhesive joint shear strength for the control EP and EP-L20 polyblend both cured at room temperature was almost the same.

[b] The thermal cure has increased the adhesive joint shear strength of the control EP only threefold, whereas it has increased that of EP-L20 about sixfold.

[c] As shown in Fig.3.3, the values of adhesive joint shear strength increase as the amount of lignin increases up to 20%, then go down.

These observations show that the beneficial effect of lignin on the adhesive joint shear strength of EP-L takes place only at elevated temperatures. It is possible that in polyblends cured at room temperature, lignin acts only as a filler, resulting in an immiscible system. While curing at elevated temperatures, the EP-L20 is miscible, which exhibits much better adhesive strength according to the polymer blending principles. It is also possible that the EP-L

FIG.4.1 THE EFFECT OF THERMAL CURING ON ADHESIVE JOINT SHEAR STRENGTH OF EP AND EP-L20



EP: CA1200-HY2992
L : Tomlinite

polyblends with up to 20% lignin, cured at elevated temperature, will be miscible and as a result, their adhesive strength will increase, while the EP-L polyblends with over 20% lignin will be immiscible and their adhesive strength will decrease.

It is known that miscibility is the most important and significant topic in the polyblend research field. Thus, miscibility of EP-L polyblends is investigated in this chapter by DSC, DMA and NMR methods [2,4].

4.2 POLYMER-POLYMER MISCIBILITY AND GLASS TRANSITION TEMPERATURE (Tg)

Miscibility of polymers was once viewed as an interesting but very rare occurrence. However, the number of miscible polymer blends reported in the literature has increased by an order of magnitude in the past twenty years with the number of technical papers in this area increasing accordingly. Polymer miscibility has become a major area of research in many industrial and academic laboratories.

Clarification of the use of the term "miscibility" to describe single-phase, polymer-polymer blends is necessary [54]. Prior studies and reviews have generally used the term "compatible" to describe single-phase behaviour. However, "compatibility" has been used by many other investigators involving various studies of polymer-polymer blend behaviour to describe good adhesion between the constituents, the average of mechanical properties, the behaviour of two-phase block and graft copolymers, and ease of blending. The term "solubility," which is more descriptive and like "compatibility," could be another choice for describing molecular mixing in polymer-polymer blends. For single-phase, solvent-solvent and polymer-solvent mixtures, solubility is the accepted term. With polymer-polymer blends, ideal or random molecular mixing may not adequately describe the true nature of the blend even though the physical parameters of the blend would suggest true solubility. The term "miscibility" has been chosen to describe polymer-polymer blends with behaviour similar to that expected of a single-phase system. The term miscibility used in this field does not imply ideal molecular mixing but suggests that the level of molecular mixing is adequate to yield the macroscopic properties expected of a single-phase material [54].

The best commercial advantages of a miscible polymer blend can be summarized by the word "versatility". Without resorting to composition changes, the number of possible variations in usable properties is limited for a specific polymer. Polymer blends offer significant property diversification. With miscible polymer mixtures, mechanical compatibility is assured and a property compromise between the constituents is therefore achieved. Thus, with a miscible polymer-polymer blend, a range of price/performance characteristics between the component polymers can lead to a large number of potentially useful and different products. This versatility places miscible polymer blends in a unique situation with potential commercial importance [54].

The most commonly used method for establishing miscibility in polymer-polymer blends is through determination of the glass transition in the blend versus the glass transition of the unblended constituents.

Polymer exhibits a certain glass transition. The viscous liquid (or flexible, rubbery material in the case of high molecular weight polymers) is transformed into a hard, glassy material upon passing through this transition.

A miscible polymer blend will exhibit a single glass transition which is between the Tg's of the components and which has a sharpness of the transition similar to that of the components. With cases of limited miscibility, two separate transitions between those of the constituents may result, depicting a component 1 - rich phase and a component 2 - rich phase.

The most frequently cited methods for determining Tg of polymers and polymer blends are calorimetric methods, such as DSC, mechanical methods, such as DMA and so on. The nuclear magnetic resonance method (NMR) is also a useful method to study the polymer-polymer miscibility on an even finer scale.

4.3 MISCIBILITY STUDY BY DSC

When the temperature of a substance is raised or lowered, physical or chemical changes may occur; for example, a transition from one phase to another, or a chemical modification. The DSC has been designed to determine the enthalpies of these changes by measuring the differential heat flow required to maintain a sample of the substance and an inert reference at the same temperature. The temperature is usually programmed to scan a temperature range with a linear increase at a predetermined rate, but the apparatus can also be used isothermally. In reviewing the literature, it is apparent that DSC is the favourite method of investigating Tg, possibly because it was the first method to furnish quantitative thermo-analytical data.

In DSC measurement, the heat flow of polymers exhibits a change when passing through the glass transition. The DSC measures the amount of heat required to increase the sample temperature by a value ΔT over that required to heat a reference material by the same ΔT. Through sophisticated instrumentation, controlled rates of heating or cooling are possible with high accuracy of heat input (or output) to small specimens.

The first application of DSC for Tg studies of epoxy resin dates back to Fava [150], who pointed out that Tg could be used as a sensitive cure index during the later stages of the cure. Abolafia [151] performed experiments on a number of epoxy resins, with different molecular weights, used for reinforced laminates. As a function of cure time and temperature, Manz and Creedon [152,153] examined the glass transition temperatures of two different epoxy resin used for printed circuitry, showing that the Tg's of both materials shift to higher values as curing temperature and time are increased.

The DSC technique has successfully demonstrated polymer-polymer miscibility for systems such as PPO-polystyrene, nitrile rubber-PVC, poly(vinyl methyl ether)-polystyrene and so on. Using DSC, Zabrzewski [154] observed that the PVC is miscible with levels of 23% to 45% acrylonitrile rubber. These results are in excellent agreement with dynamic mechanical data. Landi [155] investigated similar blends and observed single-phase behaviour in the case of nitrile rubber with a 34% acrylonitrile-content blended with PVC.

In this study, the Tg's of cured EP and EP-L polyblends were determined using a 910 DuPont DSC connected with a 1090 DuPont Thermal Analyzer. Samples were run at a constant heating rate of 20°C/min from -40 to 180°C under a nitrogen atmosphere.

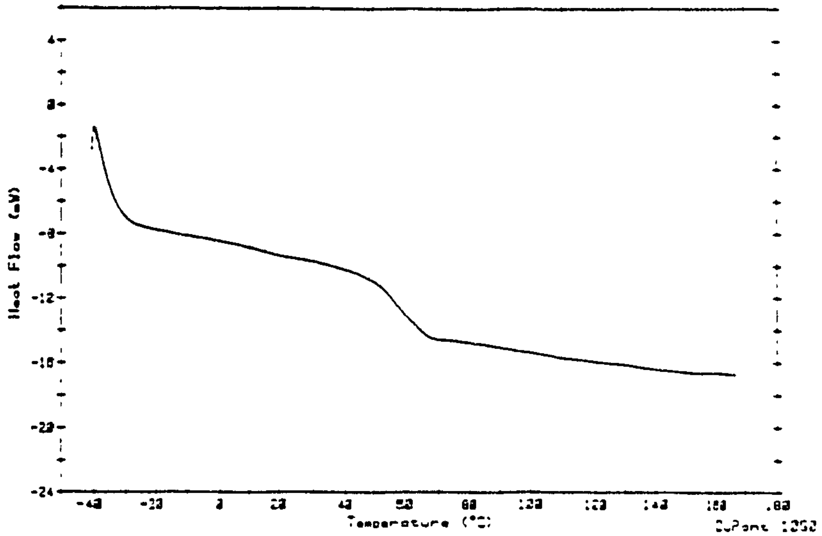
Reference and sample specimens were placed in individual cells or pans which sat on a thermoelectric disc. Heat was transferred at a constant rate to the disc and into both reference and sample via the specimen pans. The differential temperature of the specimens was monitored by area thermocouples located on the underside of the disc beneath each specimen pan. Since the thermal resistance to the specimens was held constant, differential temperatures were directly proportional to differential heat flows. At Tg, the sample temperature remained constant until the heat of transition had applied, whereas the reference specimen continued to increase in temperature causing the differential temperatures and hence a negative heat flow was observed in this region.

The DSC curves of EP and L are shown in Fig.4.2 and Fig.4.3. The effect of lignin amount on Tg of EP-L blends is shown in Fig.4.4 which indicates that there is a single Tg for both EP and EP-L20 blends thermally cured which is characteristic of monophasic systems. However, when lignin content is increased to 25% or more, EP-L polyblends exhibit two Tg's. The first Tg is close to the Tg of EP, with a tendency to increase as the lignin content increases (see Fig.4.4 and 4.5), indicating the epoxy rich phase. The second Tg is in the proximity of the Tg of lignin, indicating the lignin rich phase.

4.4 MISCIBILITY STUDY BY DMA

DMA is a technique in which the dynamic modulus and damping of a substance are measured as a function of temperature when the substance is subjected to a controlled temperature programme and under an oscillatory load.

Fig.4.2 DSC Curve of Epoxy



EP: CA1200-HY2992
Cure Condition: 100°C, 2h

Fig.4.3 DSC Curve of Lignin (Tomlinite)

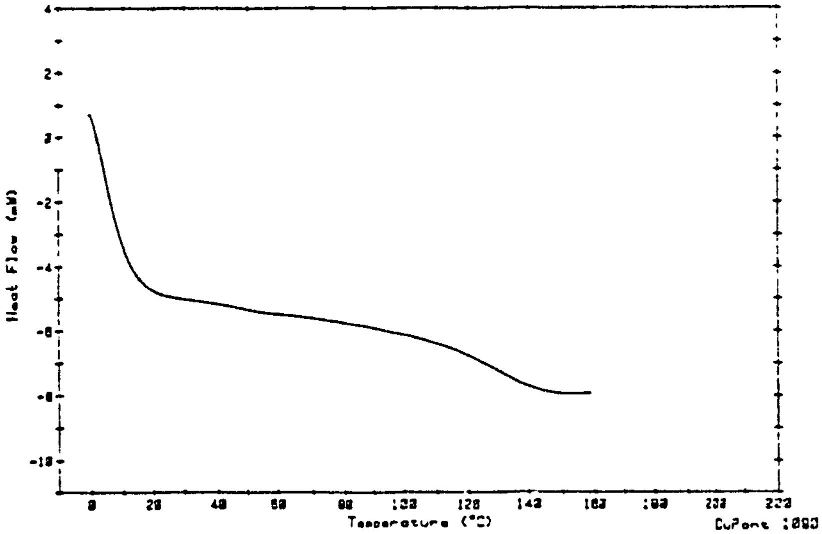
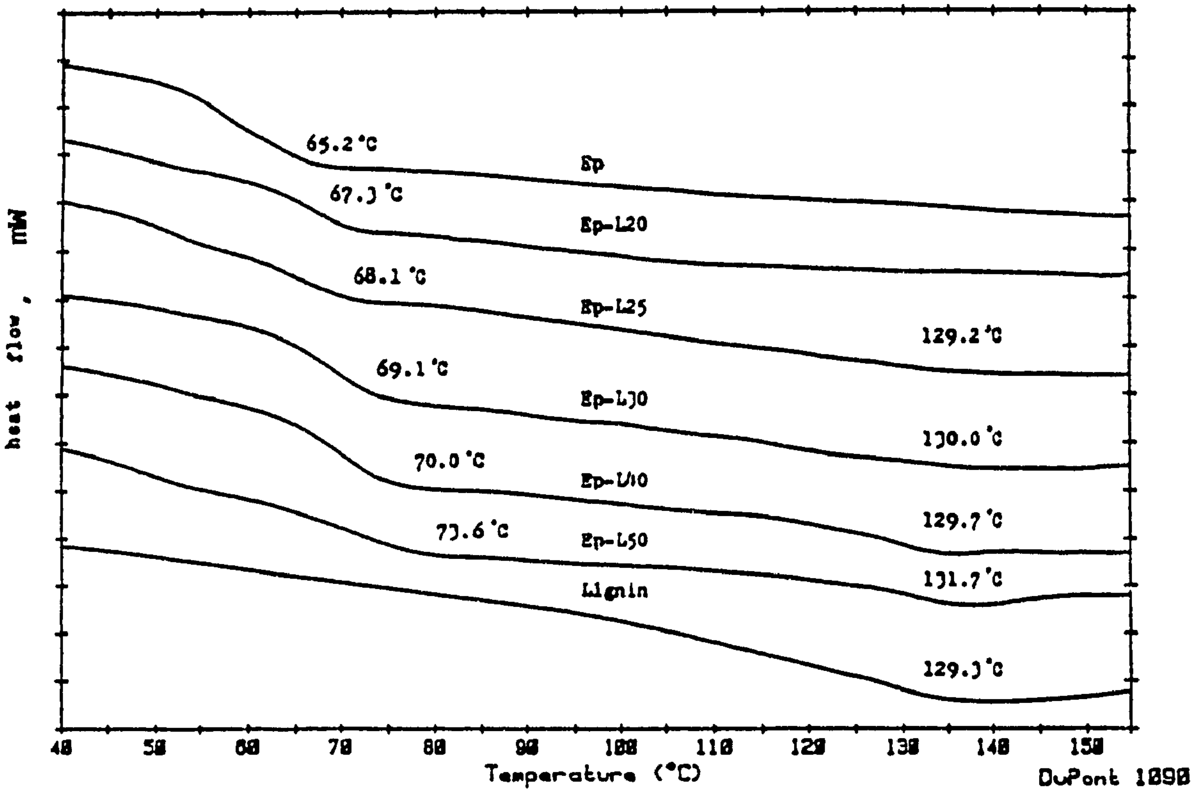
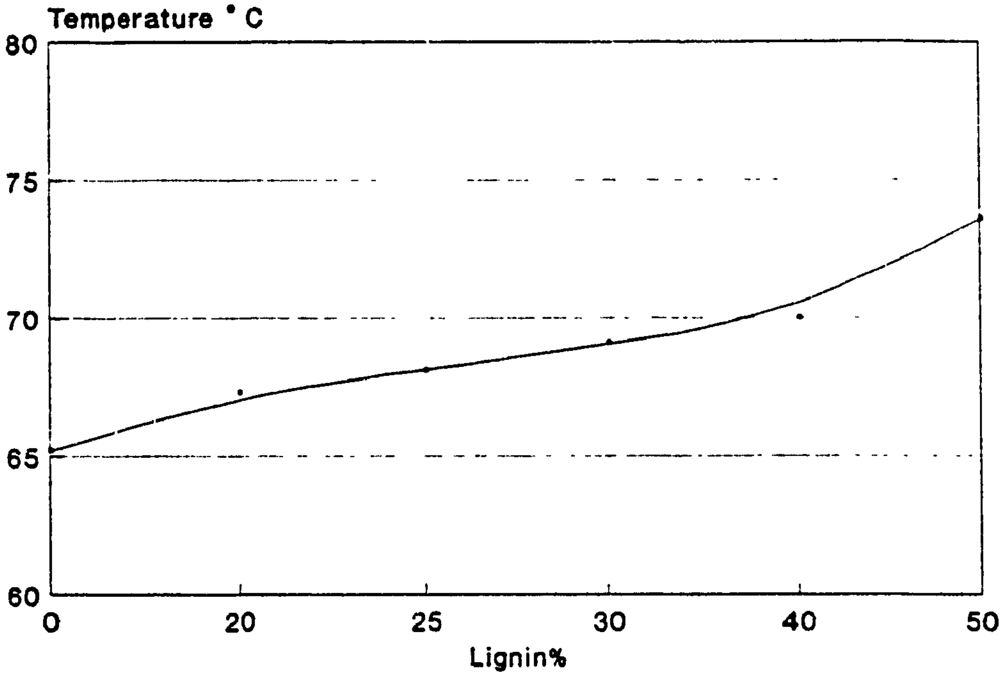


FIG.4.4 EFFECT OF LIGNIN AMOUNT ON
Tg OF EP-L BLENDS



EP: CA1200-HY2992
L : Tomlinite
Cure condition: 100 °C, 2 h

FIG.4.5 THE RELATION BETWEEN LIGNIN AMOUNT AND THE FIRST Tg OF EP-L



EP: CA1200-HY2992
L : Tomlinite

Polymers are examples of viscoelastic materials, which have some of the characteristics of both viscous liquids and elastic solids. An elastic material has a capacity to store mechanical energy with no dissipation of energy; on the other hand, a viscous fluid has a capacity for dissipating energy, but none for storing it. When polymeric materials are deformed, part of the energy is stored as potential energy and part is dissipated as heat.

The DMA yields damping and the dynamic modulus (G). The dynamic modulus (G) consists of a real part (G′) and an imaginary part (G′′) as follows:

$$G = G' + i\,G''$$

where G′ is the storage modulus, elastic modulus or energy storage term; G′′ is the loss modulus, viscous modulus or energy dissipation term; i is the symbol of the imaginary part. The mechanical loss factor, tanδ, is defined as:

$$\tan\delta = \frac{G''}{G'}$$

A large number of experimental methods has been developed in the last 30 years, but only a few of them are ready for automation and a computer-aided evaluation of the components of the complex modulus.

A new commercial mechanical spectroscope has been introduced by Blaine and co-workers [156] called 'Dupont DMA' in which a specimen is subjected to cyclic strain under forced resonance. The energy input (damping) required to maintain constant amplitude is a measure of the mechanical loss factor tanδ; the natural frequency is a measure of the storage modulus. The loss and frequency are recorded continuously.

The dynamic mechanical performance of cured epoxy resins is measured for various reasons. The measurements have proved useful in evaluating glass transitions, crosslinking density and other molecular features of the cured resins.

An early extensive study of the dynamic mechanical properties of cured epoxy resins was published by Kealble [157]. Using a Maxwell device, he studied the dynamic response of diglycidyl-ether of bisphenol-A cured with boron trifluoride amine complex, diethylene triamine, metaphenylene diamine, methylene bis(orthochloroaniline) and aliphatic diamine, in correlation with the thermal softening temperature by distortion or penetration.

Mechanical methods for determination of the transitional behaviour of polymers and polyblends have been cited more frequently than the other techniques. The elastic and viscoelastic properties of polymers derived by subjecting polymers to small amplitude cyclic deformation can yield important information concerning transitions. Data obtained over a broad temperature range can be used to ascertain the molecular response of a polymer in blends with other polymers. In a highly phase-separated polyblend, the transitional behaviour of the individual components will be unchanged. However, in a miscible blend, a single and unique transition corresponding to the glass transition will appear.

B.Tomita et al. [147] have reported on the preparation of pre-reacted, ozonized lignin/epoxy resin and the dynamic properties of the polyamine cured networks. The dynamic mechanical measurements showed complete compatibility between ozonized lignin and epoxy resins after curing with amine. It was also found that the glass transition temperatures of cured resins could be modified over wide ranges by selecting different curing agents.

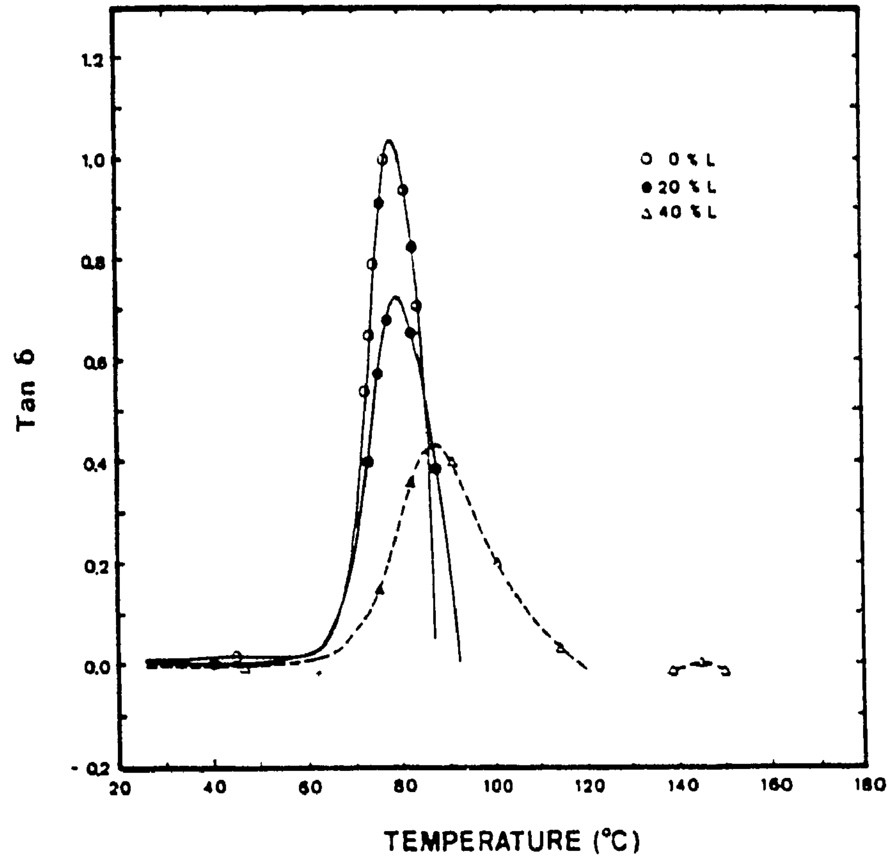
In this study, the DMA was performed on a 982 DuPont DMA connected with a 1090 DuPont Thermal Analyzer under a nitrogen atmosphere.

The DuPont 982 DMA is a free oscillating resonant instrument in which a sample is mounted between two freely oscillating pair of parallel arms to form a compound resonant system. The natural resonant frequency of this system is primarily determined by the geometry and modulus of the sample and the damping is essentially resolved by the energy dissipation within the sample. The sample is set in motion and maintained at the natural resonant frequency of the compound system by a electromechanical transducer.

The cured samples (65x12x2.5mm) were mounted between vertical clamps for quantitative results with respect to the storage modulus, loss modulus and tanδ. All measurements were carried out within the temperature interval of 20°C to 180°C.

In Fig.4.6, tanδ curves are displayed. Since EP-L20

FIG.4.6 Tan δ (DMA) vs TEMPERATURE
FOR EP AND EP-L [2]



EP. CA1200-HY2992
L : Tomlinite

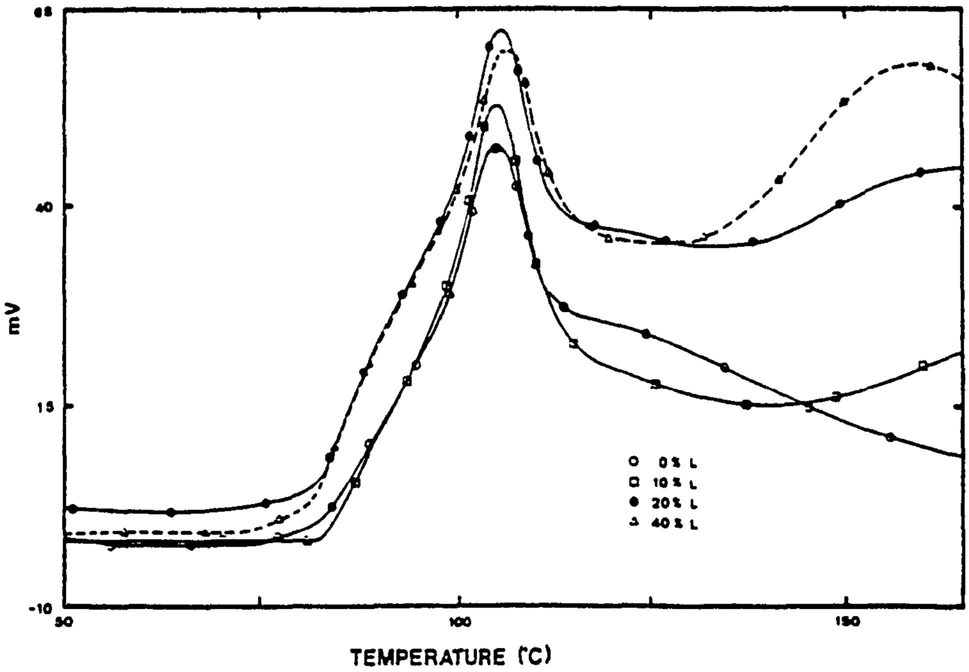
exhibits a single Tg, characteristic of a monophasic system, the blend may be considered miscible. However, for EP-L40 polyblend, a second peak on the tanδ curve is located in the temperature region characteristic of lignin motion. This indicates the immiscibility of EP-L40 polyblend.

The fact that the EP-L20 blend is miscible and the EP-L40 blend is not miscible may explain the decrease in shear strength in EP-L blends which have lignin content in excess of 20%, as shown in Fig.3.3.

The uncured EP or EP-L sample was placed on a strip of fibreglass cloth which was premounted between horizontal clamps. Our intention was to follow the progress of the curing process and its changes in frequency and damping signals and hence, to confirm whether or not the two polymers were miscible.

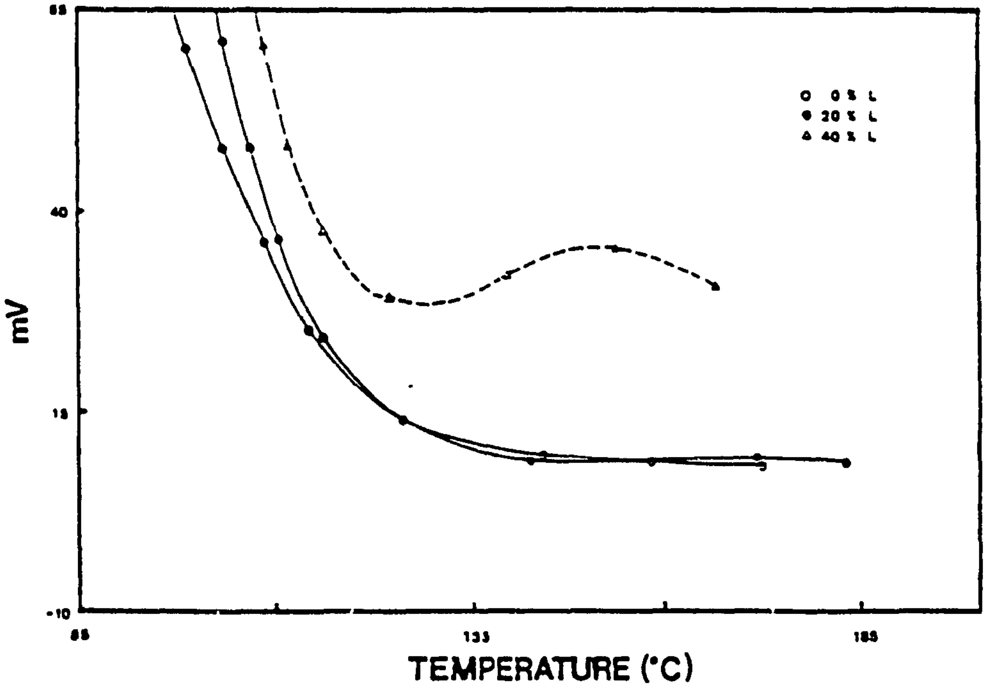
Dynamic tests were performed on a set of uncured samples from 20°C to 180°C at a heating rate of 5°C/min such that the thermal contact time between EP in the rubbery state and lignin was short. As can be seen from the right side of the damping-temperature curves (Fig.4.7), the damping signals reach a maximum at ca.106°C after which they drop off rapidly. The drop is continuous for EP, but for EP-L polyblends, second damping signal peaks appear at ca. 150°C due to lignin motions from the glassy to the rubbery state. The height of the second damping peak for EP-L polyblends can easily be correlated with the lignin content in each polyblend. It appears that almost

FIG.4.7 DMA DAMPING SIGNALS vs. TEMPERATURE FOR EP AND EP-L POLYBLENDS [2]



Heating rate: 5 °C/min.

FIG.4.8 DMA DAMPING SIGNALS vs. TEMPERATURE FOR EP AND EP-L POLYBLENDS PREVIOUSLY CURED FOR 2 h AT 100 °C [2]



Heating rate: 5 °C/min.

all of the lignin present in polyblends is free, since its presence does not change the maximum peak position of the first damping signal, which itself is associated with EP motions. The presence of a second damping peak that correlates with the glass transition of lignin indicates the immiscibility of lignin in all the polyblends which were not cured for 2 h at 100°C.

In another set of tests, the same type of samples were first isothermally cured in the DMA oven at 100°C for 2 h. These were the same conditions as in the thermal cure of the EP and polyblends. After 2 h, the samples were allowed to cool to room temperature and were then tested again. The damping signals in the lignin glass transition region were plotted in Fig.4.8 In this set of tests, the second damping peak due to lignin's Tg is not identifiable in the damping signal of EP-L20, indicating the miscibility of EP-L20 after the thermal cure but the immiscibility before thermal cure. However, for the EP-L40 polyblend, a second damping signal peak still appears after the thermal cure, thus indicating the immiscibility of the EP-L40 blend even after the thermal cure.

The fact that the EP-L20 blend is miscible after curing at 100°C for 2 h and immiscible after curing at room temperature or after only a short thermal contact time, may explain the result of the sixfold increase in shear strength of EP-L20 after thermally curing at the above mentioned conditions. Based on these findings, it is supposed that, during the thermal cure, some interaction between lignin and epoxy-polyamine exists resulting in a miscible single phase system.

4.5 MISCIBILITY STUDY BY NMR

In order to confirm the results from DSC and DMA, the NMR method was used to study the miscibility of EP-L systems. NMR, nuclear magnetic resonance, is an phenomenon caused by the resonance transitions between the magnetic energy levels of atomic nuclei in an external magnetic field [158].

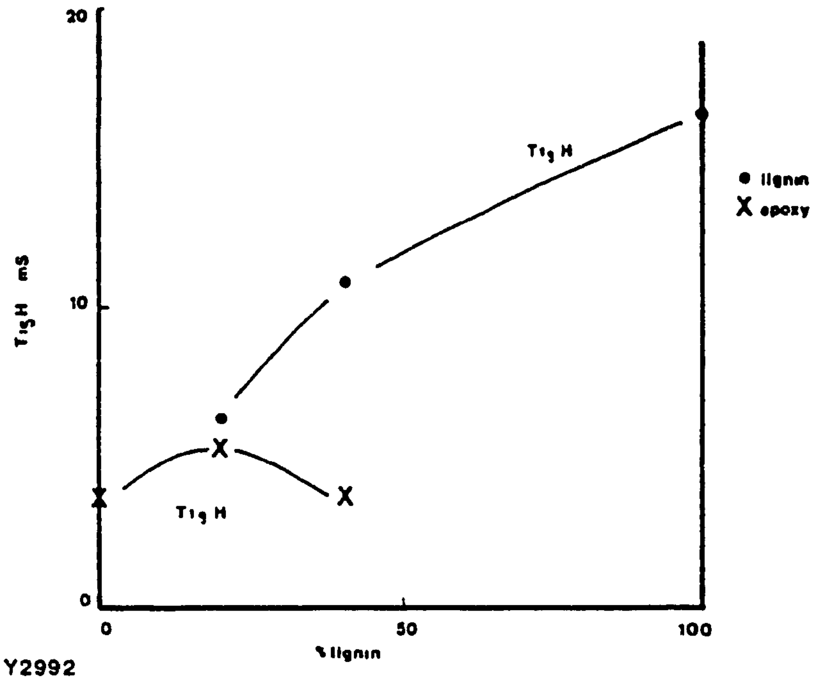
Proton NMR experiments on polymers are generally confined to studying the spin-spin and spin-lattice relaxation processes as functions of temperature and composition [54,159]. As with mechanical measurements, simpler results are expected with one-phase than with two-phase mixtures. Although the origins of the changes with the temperature of both mechanical and NMR responses are the same, the strength or intensity of the changes may be quite different between the two methods. Also, the equivalent frequency of the NMR experiment is quite high. When both mechanical and NMR methods do give information on a molecular motion, agreement is quite good[54].

One of the spin-lattice relaxation methods was proposed in 1981 by Schaefer et al [160]. It consists of measuring one relaxation parameter, the proton spin-lattice relaxation time in the rotating frame ($T_{1\rho}H$) for both individual components of the blend, and comparing the values found with the $T_{1\rho}H$ of the blend. If the two components have $T_{1\rho}H$ values that differ from one another, and an intermediate value is found for the blend, one can assume that there is molecular miscibility within the blend. $T_{1\rho}H$ can be measured on different carbon signals in the spectrum, and it is the same for every carbon when the sample is chemically homogeneous. In a phase-separated blend, one can actually measure a different $T_{1\rho}H$ value, for the carbon in each of the two phases.

In this study, the high-resolution solid-state NMR spectra were obtained on a Bruker CXP-200 spectrometer. The measurements were performed at room temperature under magic angle spinning at ca. 2.5 KHz using a cross-polarization field, and the contact time was varied as long as a signal was being obtained. From the graphs of signal intensity as a function of contact time, the rotating frame parameter ($T_{1\rho}H$) was calculated. This parameter was suggested in 1981 [160] as a probe of phase composition for blends and has since then been used in various systems.

The CP-MAS NMR spectrum of lignin was previously assigned [161] and has the most important signal at 56 ppm (for the aromatic methoxyl carbons) and at 149 ppm (for the aromatic ring carbons 3 and 4). The $T_{1\rho}H$ of all lignin signals in the conditions mentioned above is 16.5 ms. Fig.4.9 presents the $T_{1\rho}H$ signals for EP and L in control specimens and EP-L polyblends. The $T_{1\rho}H$ for the EP control is 3.7 ms.

FIG.4.9 T1pH SIGNAL FOR EP AND LIGNIN IN CONTROL SPECIMENTS AND EP-L POLYBLENDS [2]



EP: CA1200-HY2992
L : Tomlinite

The $T_{1\rho}H$ values are found to occur in polyblends corresponding to the two phases. The two values can be obtained from the signals belonging to the EP control and to the lignin, respectively. However, as can be seen in Fig.4.9. the two $T_{1\rho}H$ values are not constant over the whole composition range. The $T_{1\rho}H$ of the lignin decreases with a corresponding decrease of lignin amount in the blend. The $T_{1\rho}H$ of the epoxy, however, seems to increase for a 20% lignin content in the blend and then decrease to the initial value. With EP-L20 blend, the lignin $T_{1\rho}H$ is almost as same as the epoxy $T_{1\rho}H$, indicating that the blend may be miscible, even by NMR standards.

From the shape of the curves in Fig.4.9, it seems reasonable to assume that a stoichiometric reaction occurs at 20% lignin, generating homogeneous properties on the macroscale and creating the appearance of a homogeneous mixture even on a very fine scale (a few angstroms, as observed by NMR).

4.6 SUMMARY

A systematic investigation was conducted for thermally cured EP-L polyblends with up to 50% lignin content. DSC, DMA, and solid-state CP-MAS NMR spectra were performed to establish the miscibility of the EP-L systems.

The Tg's of the EP-L polyblends have a slight trend to increase as the lignin content increases. Only one Tg was detected by DSC and DMA for blends with up to 20% lignin content, but two Tg's for blends with higher lignin contents. Hence, the EP-L blends are miscible with lignin contents up to 20%.

The DMA scanning mode performed on uncured samples showed a damping maximum at 106°C for EP and all EP-L blends, whereas it showed the second damping peaks at ca. 150°C for the EP-L blends. The precuring of the blends at 100°C for 2 h leads to the disappearance of the second damping peak with the exception of the EP-L40, indicating that thermal cure leads to a miscible system for EP-L polyblends with up to 20% lignin.

From the shape of the proton spin-lattice relaxation time curves (calculated from solid-state NMR spectra) showing $T_{1\rho}H$ as a function of lignin content, it seems reasonable to assume that a stoichiometric reaction occurred at a blend loading of 20% lignin. The extent of the reaction was probably not sufficient for the two components to combine at the molecular level, but it was significant enough to generate homogeneous properties on the macroscale. The agreement is quite good among the results of DSC, DMA and NMR.

These findings not only reveal the basic morphology of these novel materials, but also emphasize their application in various materials fields since miscible morphology usually gives superior mechanical properties and may give these novel EP-L polyblends vast prospects of application as adhesives, coatings, plastics, composites, mortars and so on.

CHAPTER 5

INTERACTION BETWEEN THE EPOXY-POLYAMINE NETWORK AND LIGNIN

5.1 INTRODUCTION

Why does the second Tg of EP-L20 disappear after thermal curing?

How does the EP-L20 blend change from immiscible to miscible after thermal curing, resulting in the sixfold increase of adhesive joint shear strength?

A reasonable explanation for these questions could be the enhanced degree of bonding and chemical interaction between lignin and the epoxy-amine network taking place at elevated temperatures.

To confirm a chemical interaction hypothesis, proof through several different techniques is usually required. In this study, FTIR technique, chemical analysis of amine number determination, a curing kinetics study, and an extraction and UV analysis method were applied to the lignin-amine and lignin-epoxy-amine systems [1,3].

5.2 FOURIER TRANSFORM INFRARED SPECTROSCOPY

5.2.1 PRINCIPLE OF FTIR

Emission or absorption spectra arise when molecules undergo transitions between quantum states corresponding to two different internal energies. The energy difference is described by $\Delta E=h\nu$. Infrared frequencies in the wavelength range 1-50 μm are associated with molecular vibration and vibration-rotation spectra.

A beam of electromagnetic radiation, when passed through a chemical substance, is only partially transmitted. The remainder is reflected or absorbed in varying degrees, depending on the substance, and the frequency of radiation.

The absorbed energy is transferred to the atoms or molecules in the sample substance and, as a result, the particles are promoted from lower to higher energy state.

In absorption or emission spectroscopy several energy components, namely rotational, vibrational, and electronic energy are important. A significant factor in molecular energies is the existence of discrete levels for the rotational, vibrational and electronic components. Under appropriate conditions, the molecules can absorb or lose energy and change from one level to another (but cannot assume an energy level other than those aforementioned). The energy differences between electronic levels are greater than those for vibrational levels which, in turn, are greater than those for rotational levels. Thus, electronic transitions involve high energy radiation of the visible, UV and X-Ray regions, while vibrational transitions involve IR radiation and rotational transitions the relatively low energy at far-infrared radiation.

Thus the energies associated with vibrational and rotational changes are comparable to those for IR radiation and may be studied in this spectral region. While it is true that each molecular vibration involves the whole molecule, most of the energy of this is involved within a single group. As long as the rest of the molecule is neglected, a given group can be expected to absorb approximately at the same frequency in all molecules. In effect then, we may consider this group as vibrating independently of the other atoms, a situation which given rise to characteristic group absorptions. In addition to these characteristic group frequencies occur in which the energy is distributed nearly uniformly through the entire assemblage and provide a unique property of the individual molecules. These are the most useful aspects of IR spectroscopy [158].

A molecule containing N atoms has 3N normal vibration modes, including rotational and translational motions of the entire molecule. For highly symmetrical molecules with very few atoms, the entire infrared spectrum can be correlated to and explained by the vibrational modes, but even for most low-molecular-weight substances, N is too large for such analysis. Useful information can still be obtained, however, because some vibrational modes involve localized motions of small groups of atoms and give rise to absorption bands at frequencies characteristic of these groups and the type of motions they undergo.

In polymers, the infrared absorption spectrum is often surprisingly simple if one considers the large number of atoms involved. This simplicity results first from the fact that many of the normal vibrations have almost the same frequency and therefore appear in the spectrum as one absorption band and, second, from the strict selection rules that prevent many of the vibrations from causing absorptions.

FTIR is a method in which the infrared spectra is obtained by interferometric techniques with Fourier transform algorithm by computer. This greatly increases the sensitivity and accuracy of the analysis.

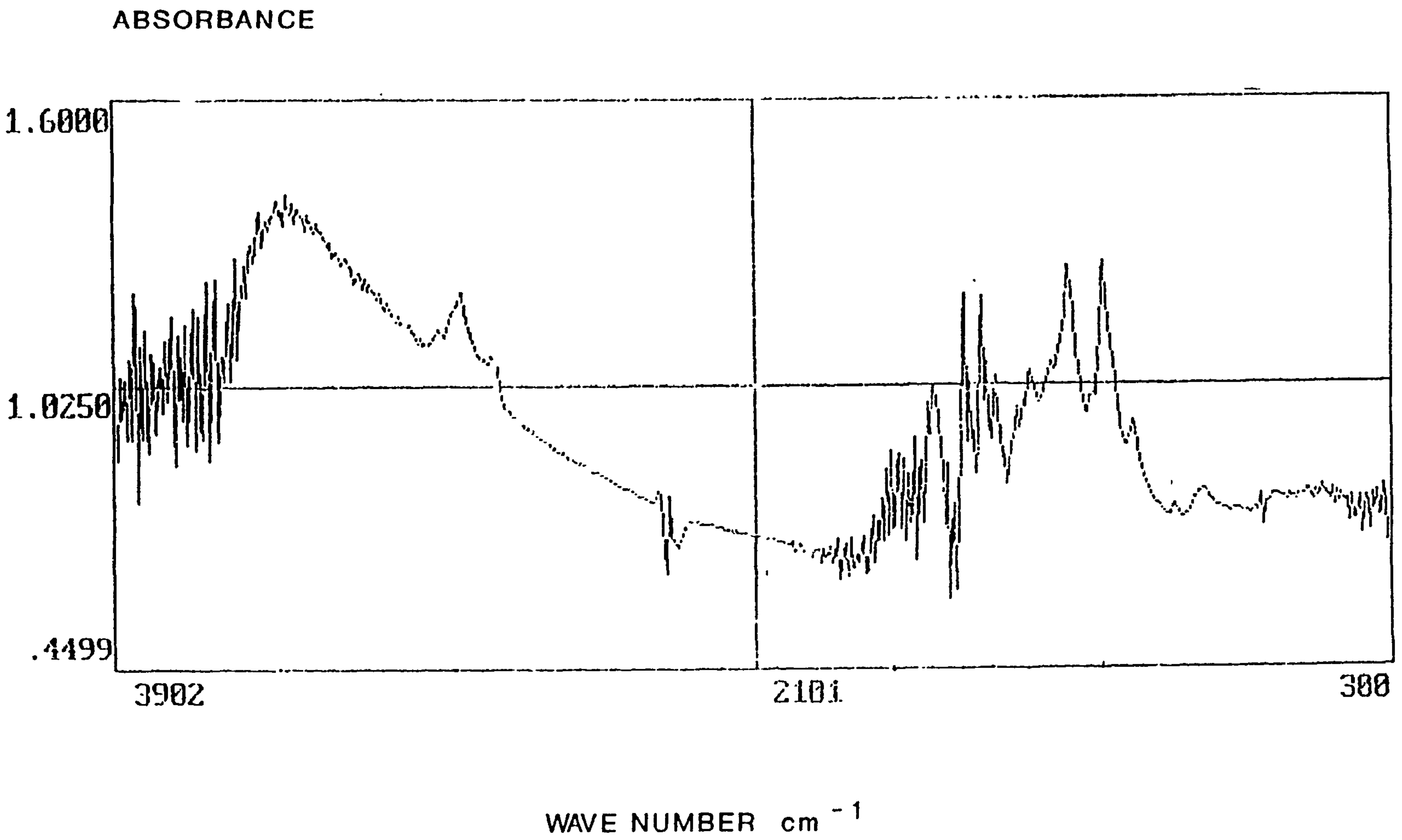
5.2.2 SPECTRA OF EPOXY AND LIGNIN

FTIR qualitative spectra were recorded on a Bomen Michelson 102 spectrophotometer between 4000 and 200 cm^{-1}. Powdered specimens mixed with potassium bromide were pressed into a disk. By using a different ratio of polyblend powder to potassium bromide (i.e., 6 mg/1000 mg for epoxy control, 7.5 mg/1000 mg for EP-L20, and so on), the epoxy concentration was always kept constant in each disk.

The FTIR spectra of the thermally cured epoxy control sample is shown in Fig.5.1. In the epoxy control spectra the characteristic bands for DGEBA epoxy prepolymer are easily recognizable [162-165]:

- C-H in epoxy: 3060 3005, 1410, 1435 cm^{-1}
- Aromatic ether: 1245 cm^{-1}
- Aliphatic ether: 1160, 1042 cm^{-1}

FIG.5.1 THE FTIR SPECTRUM OF THERMALLY CURED EPOXY (CA1200)



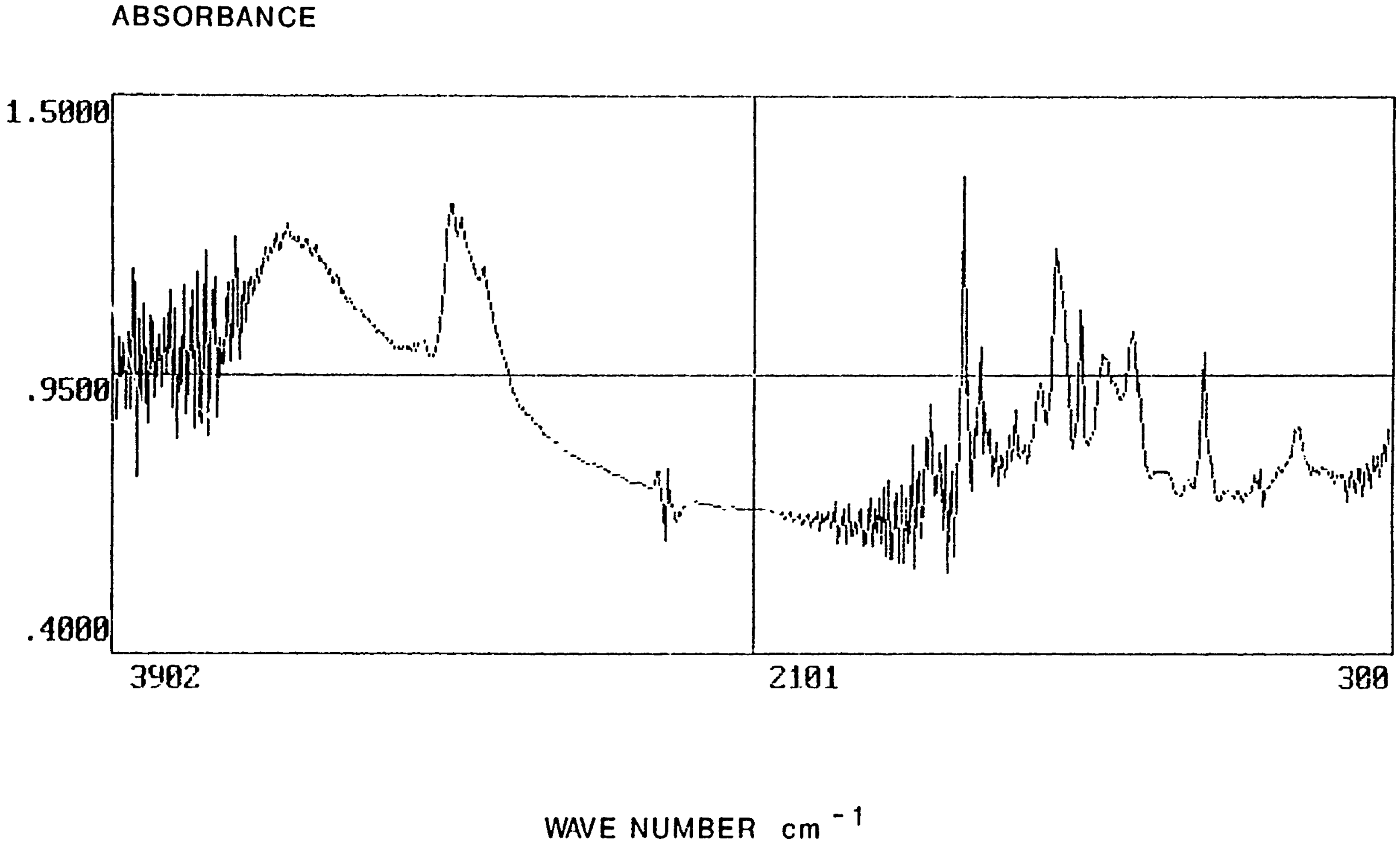
- Branched ether: 1120, 1065 cm^{-1}
- Bisphenol ring:
- C=C aromatic: 1610, 1580, 1510, 1460 cm^{-1}
- C-H aromatic: 1185, 1010 cm^{-1} , 830 cm^{-1}
- Methyl group: 2962 cm^{-1}
- Methylene group: 2860 cm^{-1}
- Geminate methyl group: 1385, 1365 cm^{-1}
- OH group: 3500-3400 cm^{-1}
- Epoxy group: 920, 870, 760 cm^{-1}.

The particular characteristic FTIR absorption bands of the lignin control sample (Fig.5.2) come from the following [166-168]:

- C=C in aromatic ring: 1610, 1510, and 1460 cm^{-1}
- Trisubstituted aromatic ring: 1150, 835 cm^{-1}
- Aromatic ring vibrations conjugated with an α carbonyl group: 1585 cm^{-1}
- Syringyl ring breathing with carbonyl stretching: 1330, 1220 cm^{-1}
- Ether linkages: 1145, 1040 cm^{-1}
- C-H aliphatic stretching and bending in methyl, methylene and methoxyl groups: 2940, 2850, 1478 and 1370 cm^{-1}
- OH groups: 3400-3500, 1370, and 1043 cm^{-1}.

The visible broad shoulder between 1750 and 1650 cm^{-1} could result from acid or ester carbonyl groups (1725 cm^{-1}), carbonyl stretching (1725-1650 cm^{-1}), aldehyde or ketone carbonyl (1669 cm^{-1}) [169-170].

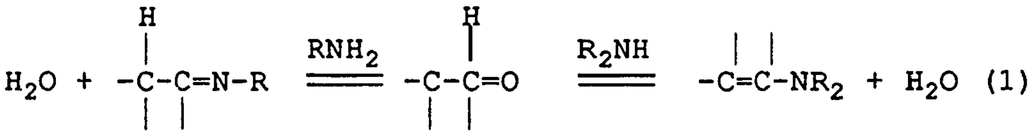
FIG.5.2 THE FTIR SPECTRUM OF
KRAFT LIGNIN (TOMLINITE)



5.2.3 SPECTRA OF LIGNIN-AMINE BLEND

It is suggested that the lignin bonding to the epoxy-amine network via traces of unreacted amine groups, which can occur only at elevated temperatures, is responsible for the improved adhesive properties of EP-L polyblends. Therefore, the FTIR study was directed toward the detection of chemical changes in lignin induced by its reaction with the polyamine hardener.

From all the functional groups present in lignin, the carbonyl groups which comprise about 5%, seem to be the most susceptible to react with amine (secondary and primary). The reaction between carbonyl compounds and amine is illustrated in the following equation [171]:



$$H_2O + -\overset{\overset{H}{|}}{\underset{|}{C}}-\underset{|}{C}=N-R \overset{RNH_2}{\rightleftharpoons} -\overset{\overset{H}{|}}{\underset{|}{C}}-\underset{|}{C}=O \overset{R_2NH}{\rightleftharpoons} -\overset{|}{C}=\overset{|}{C}-NR_2 + H_2O \quad (1)$$

The reaction product with primary amine having C=N-R double bond is an imine and that with secondary amine having $C=C-NR_2$ double bond is an enamine [171].

The detection of the chemical changes in lignin induced by its reaction with the amine hardener was carried out on a lignin-polyamine hardener (HY 2992) mixture with a ratio 1.08:1, i.e., the same ratio as in an EP-L20 polyblend. A thin film of this mixture on a potassium bromide disk was scanned after preparation as shown in Fig.5.3(A).

After scanning, the same film was cured for 1 hour at 100°C, cooled down, and then rescanned as shown in Fig.5.3(B).

FTIR also provided the difference spectrum (Fig.5.3(C)) by subtracting the spectrum before thermal cure from that after thermal cure. The common features in the spectra were cancelled and only the change was recorded. In principle, any chemical change that occurs to an extent exceeding the limits of detectability of the FTIR spectrometer should be manifested in the difference spectrum. Changes of intensity observed in the difference spectrum at a particular frequency represent the sum of the individual changes occurring in the different bands absorbing at that frequency. As shown in Fig.5.3(c), the difference spectrum indicates the following features:

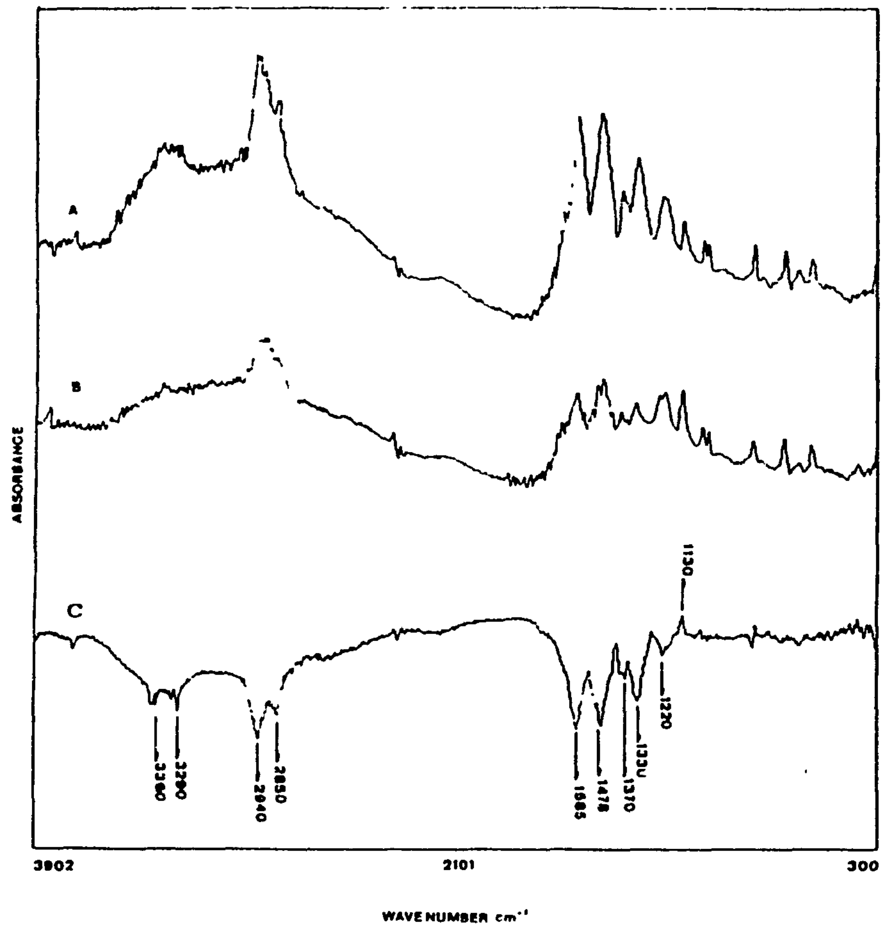
[a] Negative absorbance at 3360 and 3290 cm^{-1}:

These peaks can be attributed to N-H stretching vibrations in amine [168] The negative absorbance is an indication of the loss of the amine during the reaction with lignin, occurring at 100°C;

[b] Negative absorbance at 1585, 1330 and 1220 cm^{-1}:

The absorption at 1585 cm^{-1} can be attributed to aromatic ring vibrations conjugated with an α carbonyl group [167]. The 1330 and 1220 cm^{-1} absorbance are attributed to syringyl ring breathing with carbonyl stretching [166]. All of these bands are indirectly related to some of the lignin carbonyl groups. Consequently, their negative absorbance is an effect of the

FIG.5.3 DIFFERENCE FTIR SPECTRA OF LIGNIN-POLYAMINE (1:1.08) (BEFORE AND AFTER THERMAL CURE) [1]



A- before thermal cure
B - after thermal cure
C - difference spectrum

loss of the carbonyl groups;

[c] Negative absorbance at 2940, 2850, 1478 and 1370 cm^{-1}:

These bands designate aliphatic C-H stretching and bending in methyl and methylene groups in lignin. It is not possible to distinguish C-methyl, methoxyl, or methylene C-H in these bands. However, it seems likely that the intensities of these bands are affected by geometry and electronic effects [169]. It is obvious that even a partial replacement of the carbonyl groups in lignin's basic structure will induce changes in electronic effects and consequently changes in the intensities of the above mentioned bands.

The difference spectrum of the lignin-polyamine mixture before and after thermal treatment disclosed a diminution of the amine groups in polyamine and the carbonyl groups in lignin induced by thermal treatment. This has provided information concerning the structural changes arising in lignin and confirmed that these changes, which take place only during thermal treatment, are a result of lignin reacting with polyamine hardener. Further quantitative data concerning the lignin-amine reaction were obtained by chemical and thermal analyses. The implication of these data will be discussed later.

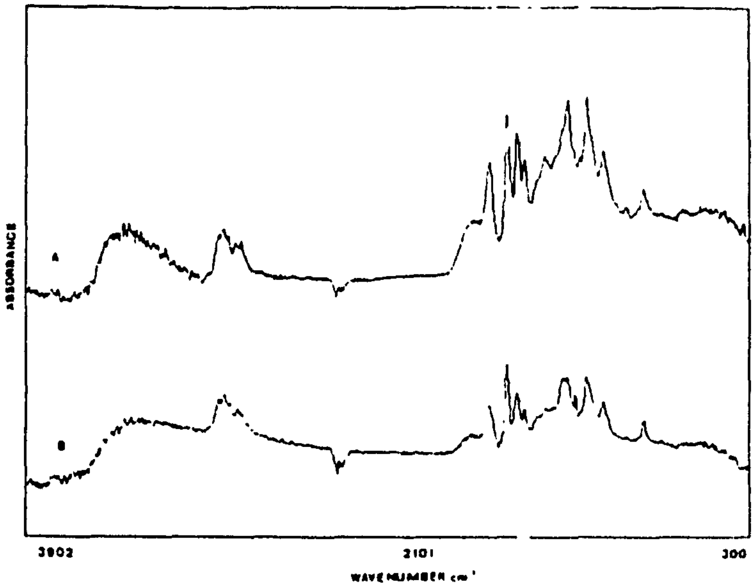
5.2.4 SPECTRA OF LIGNIN-EPOXY-POLYAMINE BLENDS

In order to see if the lignin took part in the reaction in lignin-epoxy-polyamine systems as it did in the lignin-polyamine system, the spectra of lignin-epoxy-polyamine blends were studied.

Fig.5.4 shows the difference spectra obtained after digital subtraction of the epoxy control spectrum from the EP-L20 spectrum (Fig.5.4(A)) and also from the EP-L40 polyblend spectrum (Fig.5.4(B)). Both EP and EP-L polyblends were cured at room temperature. The EP common features in the spectra were cancelled by subtraction and the absorbance of lignin which was present in EP-L blends was recorded. As expected, the spectra of lignin present in polyblends is similar to the spectrum of the control lignin (Fig.5.2), and one can assume that there is no chemical interaction between lignin and the epoxy-amine system in the room temperature curing process.

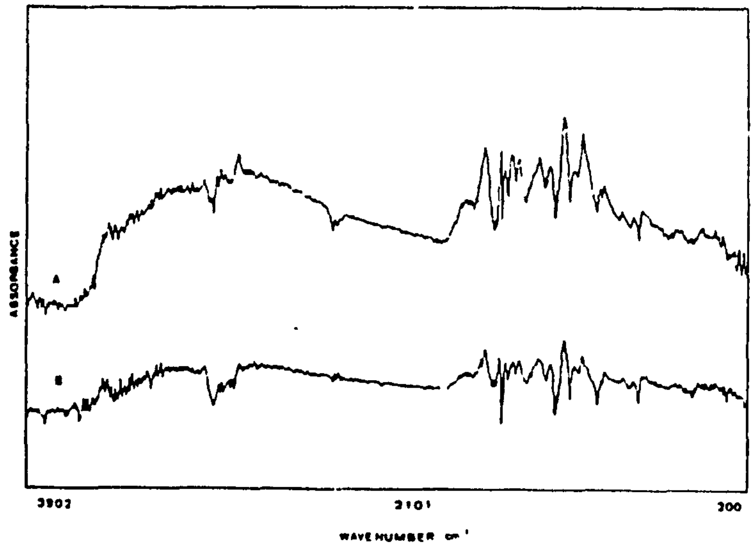
In Fig.5.5, curves (A) and (B) present the same difference spectra but in this case both EP and EP-L polyblends were thermally cured. The difference spectra again are records of the absorbance of lignin which is present in the polyblends. It is not surprising that this time the spectra are no longer similar to the lignin control spectrum. In spite of the fact that it is difficult to identify the changed absorptions due to the superimposition of absorption, it is clear that the chemical structure of lignin changed. Consequently the lignin took part in the chemical reaction during thermal cure of epoxy-amine-lignin blends.

FIG.5.4 DIFFERENCE FTIR SPECTRA OF EP-L POLYBLENDS,EP CONTROL CURED AT ROOM TEMPERATURE [1]



A - subtract EP from EP-L20
B - subtract EP from EP-L40

FIG.5.5 DIFFERENCE FTIR SPECTRA OF EP-L POLYBLENDS,EP CONTROL THERMALLY CURED[1]



A - subtract EP from EP-L20
B - subtract EP from EP-L40

5.2.5 SUMMARY OF FTIR STUDY

The FTIR spectra clearly indicate the feasibility of a reaction between lignin and polyamine hardener in an EP-L system through their carbonyl and amine groups, respectively, and that this can occur only at elevated temperatures. Part of the lignin spectral changes induced by this reaction are evident in difference spectra obtained from thermally cured EP-L polyblends and the epoxy control, whereas none of them are identifiable in the difference spectra resulting from room temperature cured polyblends and the epoxy control.

5.3 QUANTITATIVE DATA CONCERNING THE REACTIVITY OF LIGNIN TOWARDS THE POLYAMINE HARDENER

A chemical method was employed to determine the quantitative data concerning the reactivity of lignin towards the polyamine hardener as a function of temperature. This was indicated by the determination of the hardener's amine number. The amine number is represented by mg KOH which is equivalent to a 1 g hardener sample.

Several mixtures of lignin-polyamine were prepared with a lignin:polyamine ratio similar to the ratio in the EP-L10, EP-L20 and EP-L40 blends respectively. After preparation, the blends were kept in a forced circulation oven at 100°C for 2 hours. Their amine number was determined by titration [172].

The results of titration are illustrated in Table 5.1. Data from this table disclose that the reactivity of the lignin-amine system is enhanced by thermal treatment, as the amine number of the mixture is lower than the value corresponding to the equivalent quantity of amine in the mixture. At room temperature the system appears to be chemically inactive as the amine number of the mixture is similar to that of the corresponding quantity of polyamine.

These results confirm the conclusion from FTIR study, i.e., the lignin chemically reacts with polyamine hardener in the thermal cure condition but not at room temperature.

Table 5.1
Amine Number Data for the L-H Blends [1]

Amine Number (mg KOH/g)							
		Without Thermal Treatment			With Thermal Treatment		
Ratio L-H	Calculated as Function of Hardener Content	Deter-mined	mg*	%**	Dete-rmin-ed	mg*	%**
0:1	608***	-	-	-	-	-	-
0.48:1	410	411	+1	-	387	-23	-5.6
1.08:1	295	292	-3	-	257	-38	-13
2.89:1	166	-	-	-	144	-22	-13

* Difference value between determination and calculation (in mg)

** Difference value between determination and calculation (in %)

*** Determined value

5.4 KINETICS

5.4.1 THEORY AND CALCULATION (BORCHARDT AND DANIELS PROGRAM)

DSC kinetics (Borchardt and Daniels program [173]) was applied to study the chemical reaction of lignin-amine systems.

The method assumes that the reaction follows n^{th} order kinetics, i.e., it obeys the following general rate equation:

$$d\alpha/dt = k(T)(1-\alpha)^n \qquad (1)$$

where $d\alpha/dt$ = reaction rate (1/sec)

α = fractional conversion (dimensionless)

$k(T)$ = specific rate constant at temperature T (1/sec)

n = reaction order (dimensionless)

The method also assumes that the temperature dependence of the reaction rate constant, k(T), follows the Arrhenius expression:

$$k(T) = Ze^{-E/RT} \qquad (2)$$

where Z = pre-exponential factor or Arrhenius frequency factor (1/sec)

E = activation energy (J/mole)

R = gas constant (8.314 J/mole·K)

T = absolute temperature (K)

Taking logarithms of Equation 2 yields:

$$\ln k(T) = \ln Z - E/RT \qquad (3)$$

A plot of ln k(T) versus 1/T (Arrhenius plot) should be a straight line. The activation energy and pre-exponential factor can be obtained from the slope and the intercept respectively.

Substituting Equation 2 into Equation 1 yields:

$$d\alpha/dt = Ze^{-E/RT}(1-\alpha)^n \qquad (4)$$

Taking logarithms of Equation 4 produces:

$$\ln (d\alpha/dt) = \ln Z - E/RT + n \ln (1-\alpha) \qquad (5)$$

Equation 5 may be solved with a multiple linear regression of the general form $z=a+bx+cy$.

The LSC exotherm is used to measure the two basic parameters ($d\alpha/dt$ and α) required to solve Equation 5. The method assumes that the heat evolved in a small time interval is directly proportional to the number of moles reacting during that time. The reaction rate is obtained by dividing the peak height (dH/dt) at temperature T by the total heat of the reaction:

$$d\alpha/dt = (dh/dt)/\Delta H_o \qquad (6)$$

where ΔH_o = the total peak area or the theoretical enthalpy. The fractional conversion is obtained by measuring the ratio of the partial area, ΔH_T, at temperature T to the total peak area:

$$\alpha = \Delta H_T/\Delta H_o \qquad (7)$$

5.4.2 EXPERIMENT AND RESULTS

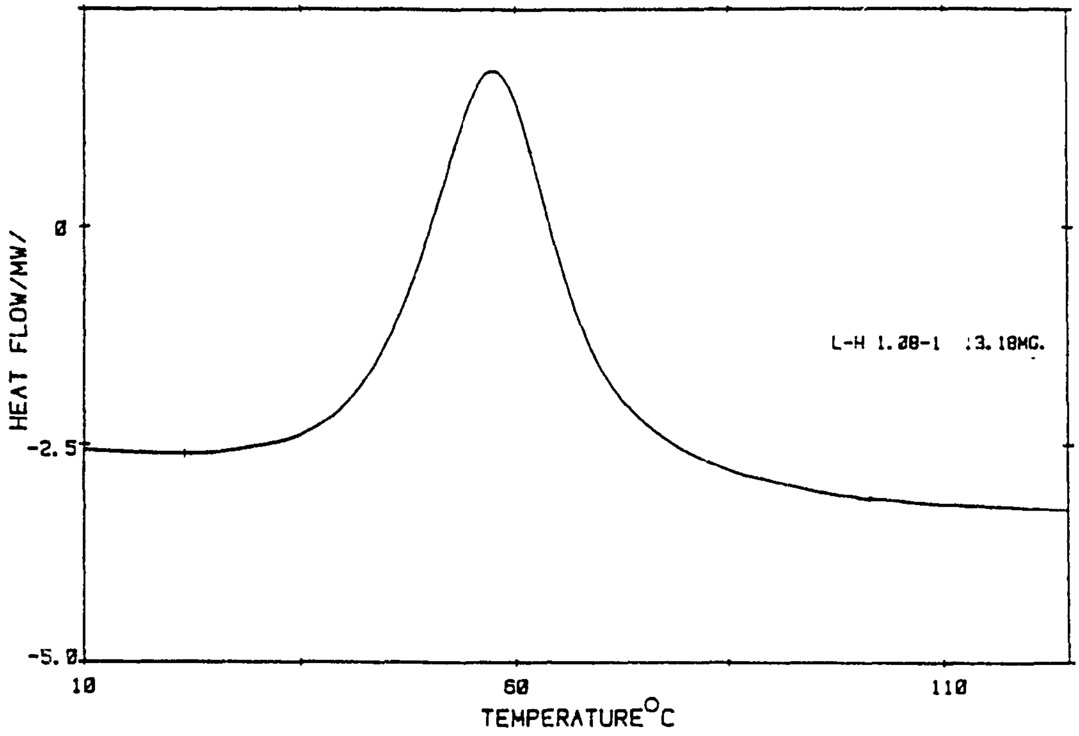
The activation energy of the reaction between lignin and polyamine hardener or epoxy and polyamine was determined. The mixture of lignin-amine was prepared with the lignin-amine ratio corresponding to the ratio in EP-L20 polyblend. Then the kinetic data was investigated using the DSC technique with a single dynamic scan. A DuPont 910 DSC connected with a DuPont 1090 thermal analyzer was used for the dynamic scans at a heating rate of 10°C/min. The DSC cell was calibrated with Indium.

The mixture of the lignin-amine for the DSC scans was prepared by thoroughly mixing the required components just before the start of the scan. About 8-10 mg of the mixture was used. The kinetic data was obtained using the DuPont, Borchardt and Daniels kinetic program.

Fig.5.6 shows results of dynamic run which was carried out at a single heating rate of 10°C/min, in the temperature range from 10°C to 110°C.

The kinetic result clearly shows that there is a exothermal chemical interactions between lignin and polyamine hardener. The activation energy was calculated from the curve in Fig.5.6 and by Equation 5. The activation energy value of lignin-amine is 154 kJ/ mol, which is more than twice higher as that of epoxy-amine control (70.3 kJ/mol). This indicates that the lignin-amine reaction cannot compete with the epoxy-amine reaction.

FIG.5.6 DSC SCAN FOR
LIGNIN-PCLYAMINE BLENDS [1]



5.5 EXTRACT OF EP-L POLYBLENDS AND DETERMINATION OF THE BONDED LIGNIN

5.5.1 SCHEME

In order to confirm the chemical bonds between lignin and the epoxy-amine network in thermal cured EP-L polyblends, UV analysis was applied on EP-L polyblend extracts.

First, the EP-L sample was extracted by dioxane-water solution. Unbonded lignin was extracted from the EP-L samples. The lignin concentration in the extract was determined by UV analysis. The degree to which lignin was chemically bonded to the polymer network was calculated from the lignin concentration data.

5.5.2 EXTRACTION

For determining the extractibility of lignin from EP-L polyblends, a suitable amount of powder (containing about 4 mg of lignin) was weighed on a Sartorius 4501 microbalance (accuracy of ±0.005 mg), placed in a flask with 20 ml dioxane-water (9:1 by volume), and then refluxed with constant stirring for 10 hours. The undissolved material was quantitatively filtered off and washed with dioxane-water in a 50 mL volumetric flask. The filtrate was then diluted to the 50 mL mark and thoroughly shaken. For UV analysis, a 10-mL aliquot was diluted to 25 mL with the same solvent.

5.5.3 UV SPECTROSCOPY

UV spectra were recorded on a Perkin-Elmer 552 UV-VIS spectrophotometer from 400 to 190 nm in 1-cm silica cells using dioxane-water (9:1 by volume) as solvent.

First, the lignin characterization in UV was done in accordance with procedures given in the literature concerning the study of different kinds of lignin in UV [174-176]. The UV absorption spectra of lignin solutions in dioxane-water show a characteristic maximum at 277 nm as shown in Fig.5.7. Free and etherified hydroxyl groups contribute to this characteristic absorption [174,175].

The absorbance at 277 nm was used to establish the calibration curve for lignin in the dioxane-water solution as shown in Fig.5.8. Its characteristic absorptivity was found to be 22.07 A L/g·cm. This absorptivity value was used to determine the lignin concentration in EP-L polyblend solutions prepared according to the previous subsection. The solutions were scanned versus a corresponding blank solution of the EP control sample prepared in the same way as the EP-L polyblend samples.

5.5.4 EXTRACTIBILITY OF LIGNIN FROM EP-L POLYBLENDS

The degree to which lignin is chemically bonded to the polymer network was calculated from the lignin concentration of the extract. The results are illustrated in Fig.5.9. These

FIG.5.7 UV SPECTRUM OF LIGNIN [1]

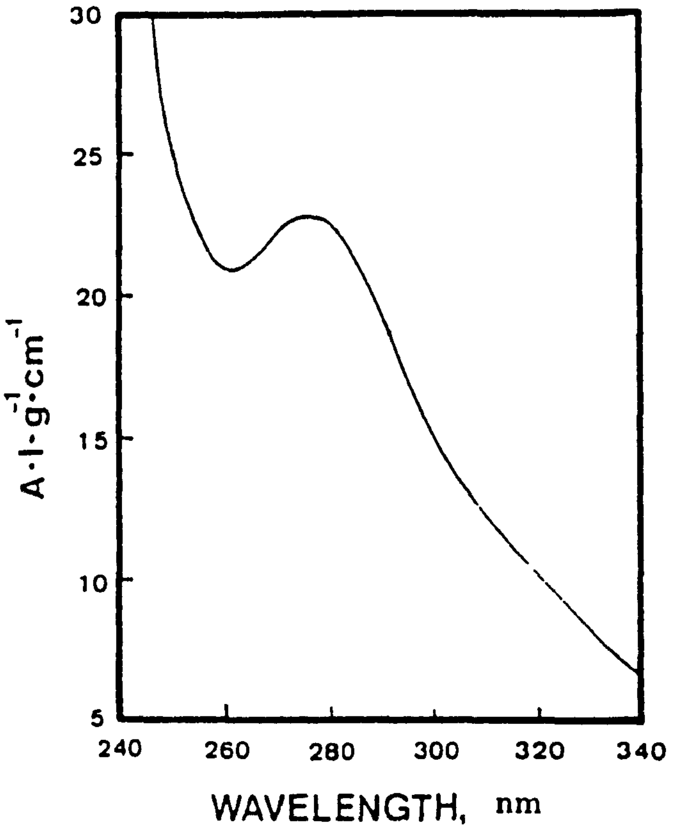


FIG.5.8 UV CALIBRATION CURVE
FOR LIGNIN AT 277 nm [1]

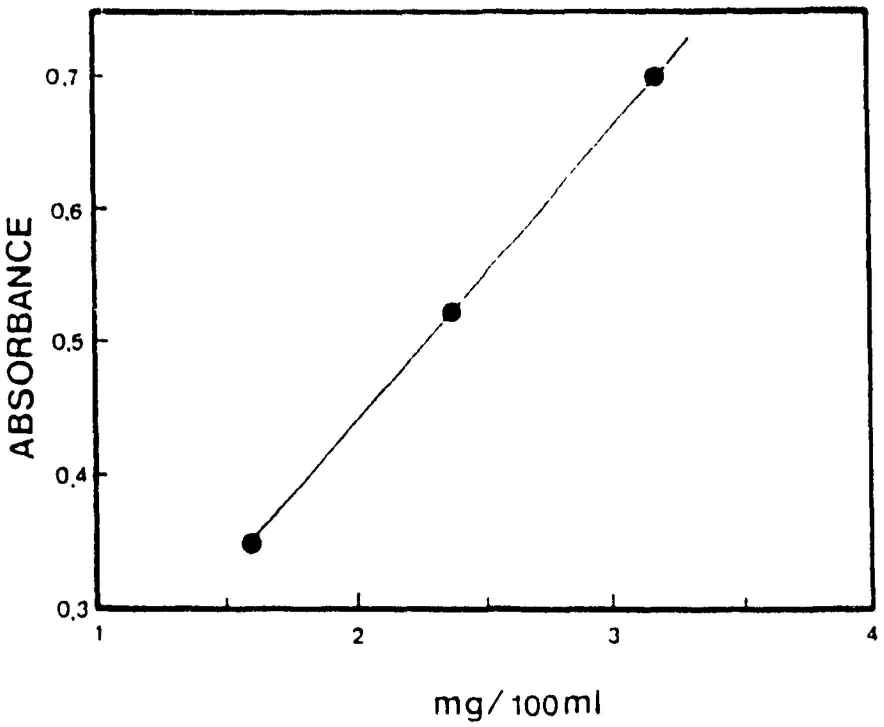
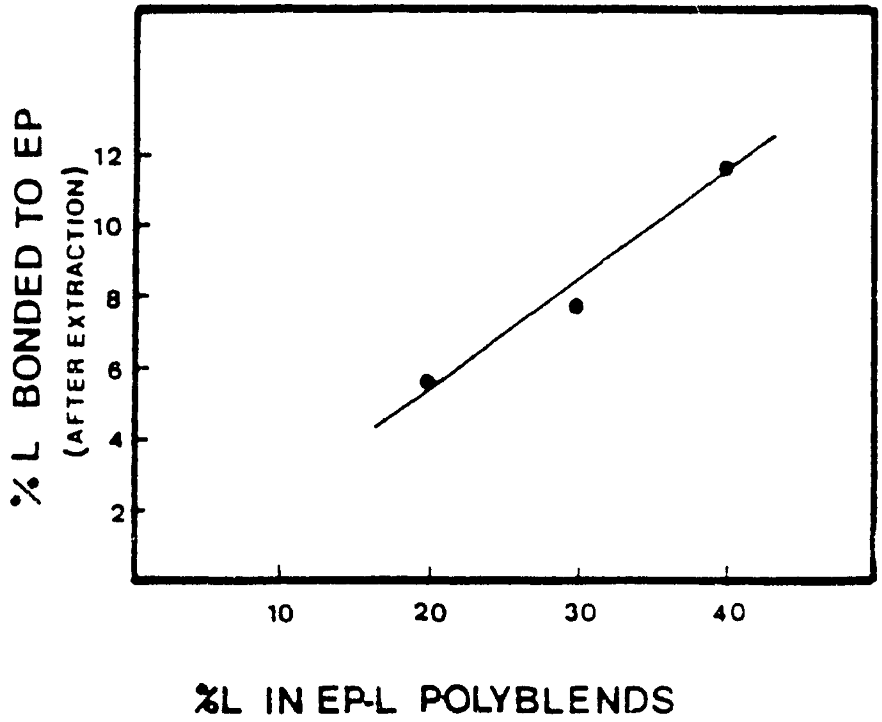


FIG.5.9 EXTRACTIBILITY OF LIGNIN FROM THE THERMALLY CURED EP-L POLYBLENDS [1]



data disclosed a proportional relationship between the percentage of lignin irreversibly bonded to the EP network during the curing process and its content in polyblends. Consequently, one may consider with justifications that the bonding of lignin to the epoxy-amine network occurs in thermal cured EP-L polyblends.

5.6 SUMMARY

In this chapter, the FTIR spectra clearly indicate the suggested chemical reaction between lignin and polyamine hardener through their carbonyl and amine groups respectively, which can occur only at thermal cure condition for EP-L blends.

Quantitative data concerning the reactivity of lignin towards the polyamine hardener have been determined by a chemical titration method.

Kinetic data indicated that during the EP-L polyblend crosslinking process the reaction between lignin and polyamine can not compete with the main reaction of epoxy groups with primary and secondary amine.

Extraction data support the supposition of lignin bonding to the epoxy-amine network via unreacted amine groups of the hardener.

The lignin bonding to the epoxy-amine network leads that the EP-L20 transforms from an immiscible blend to a miscible one [158], resulting in the sixfold increase in adhesive joint shear strength.

CHAPTER 6

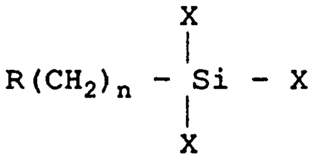
EP-L BLENDS MODIFIED BY SILANE COUPLING AGENTS

6.1 INTRODUCTION

Silane coupling agents are generally low molecular weight multifunctional compounds which can chemically couple two different phases in a composite material. Coupling agents possess the potential to form water stable covalent bonds across the substrate/polymer interface; this chemical bonding can greatly increase the durability of the bond [177-179].

Silane coupling agents have been used to improve the bond between inorganic reinforcements and organic matrix resins in reinforced plastics [180]. Plueddemann [181] and others [182-184] have shown that silane coupling agents can also enhance the durability of metal/epoxy joint and coating systems. Walker [185] used silane coupling agents in aluminum/epoxy paint systems. Various silane coupling agents were also tested on steel, cadmium, copper and zinc. In accelerated weathering exposure tests, it was found that several of the silanes could also enhance the adhesive strength and durability in metal/epoxy paint systems [185].

The organofunctional silanes can be represented by the following structural formula:



$$R(CH_2)_n - \overset{\overset{X}{|}}{\underset{\underset{X}{|}}{Si}} - X$$

where R represents a reactive organic function attached to the terminal carbon of the methylene chain bonded to silicon and X represents a readily hydrolysable group.

This dual organic-inorganic functionality permits an improvement in bonding between inorganic substrates and organic resins. In this way, it is possible to improve the strength and adhesion of resins.

It is generally accepted that the increased durability is due to the successful formation of strong covalent bonds across the metal/epoxy interface. The hydrolysable groups (X) of silicon may react with surface hydroxyl groups on the metal surface to form M-O-Si bonds [186-188], while the R group may react with the epoxy-hardener resin at the silane/epoxy interface to complete the chemical couple.

In the study [3,5] presented in this chapter, selected organofunctional silanes were employed to modify the new EP-L adhesive in order to improve the adhesive strength and the durability of the EP-L/metal bond.

6.2 MATERIALS AND PROCEDURES

6.2.1. MATERIALS

6.2.1.1 EPOXY POLYMER

An unmodified epoxy resin was used in the studies presented in Chapters 6 and 7. This unmodified liquid epoxy resin, Araldite GY6010, from Ciba-Geigy, is based on bisphenol-A and epichorohydrin.

Typical properties:

Weight per epoxy	182-192
Viscosity @25 °C	12,000-16,000 Cp

Triethylenetetramine (TETA) was used as hardener.

The stoichiometric mixing ratio between epoxy and hardener was 100:12.

6.2.1.2 LIGNIN

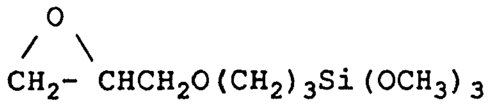
The Tomlinite lignin is the same as that mentioned in Chapter 3.

6.2.1.3 SILANES

Three types of organofunctional silanes from Union Carbide were used: A-187, A-1110, and A-189.

[a] A-187

A-187 is a glycidoxypropyltrimethoxysilane with the following formula:



$CH_2-CHCH_2O(CH_2)_3Si(OCH_3)_3$

Mw: 236.4

Specific Gravity: 1.069

[b] A-1110

A-1110 is a aminoalkylsilane with the following formula:

$H_2NCH_2CH_2CH_2Si(OCH_3)_3$

Mw: 179.3

Specific Gravity: 1.014

[c] A-189

A-189 is a mercaptopropyltrimethoxysilane with the following formula:

$HSCH_2CH_2CH_2Si(OCH_3)_3$

Mw: 196.4

Specific Gravity: 1.057

6.2.2. PREPARATION OF POLYBLENDS

The blends were prepared by manually stirring the epoxy prepolymer and lignin (10% by weight) at room temperature for two minutes; then the equivalent quantity of polyamine hardener and silane were added and stirred for five minutes at the same temperature.

6.2.3. SHEAR STRENGTH TEST

The aluminum substrates were abraded and then cleaned with acetone. Single-lap shear joints were used for evaluating the adhesive shear strength by tension loading (ASTM D-1002) as described in Chapter 3.

6.2.4 WATER RESISTANCE AND UV EXPOSURE

In the water resistance test, the shear strength was determined on cured specimens which had been immersed in water at 23°C for 630 hours.

The UV exposure conditions were as follows: 400 W UV lamp at a distance of 15 cm from the specimens with an exposure time of 700 hours. The environmental temperature was 50±3°C.

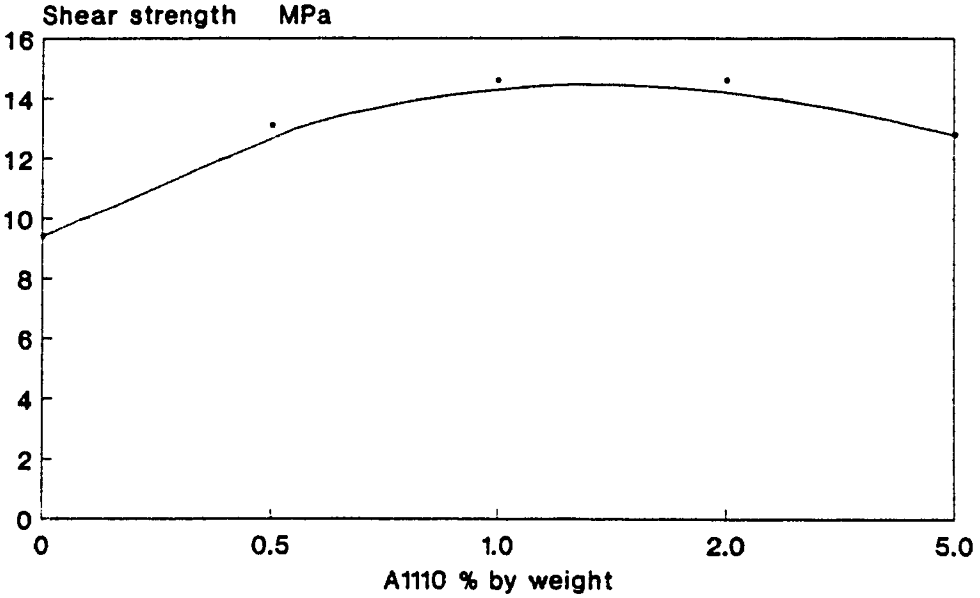
6.3 SILANES AS EP-L BLEND ADDITIVES

6.3.1 SILANE CONCENTRATION

Organofunctional silane can be applied either as a thin film on the substrate (Primer method), or as an additive to the resin system (Blend method). The blend method, which was employed in this study, seems to be a simpler technique for EP-L adhesive, because it is very convenient to add the silane at the same time as the lignin is added to the resin.

Fig.6.1 shows the effect of the silane (A-1110) concentration (based on the blend weight) on the adhesive bond

Fig.6.1 Effect of the silane concentration on adhesive joint shear strength of EP-L10-A1110



EP: GY6010-TETA
L10: Tomlinite lignin,10%

shear strength of EP-L10-A1110/aluminum joint. The appropriate amount of silane seems to be 1-2% of the blend by weight. Practical experience indicates that only a very small amount of silane at the interface is sufficient to provide marked improvement in adhesive strength.

6.3.2 EFFECT ON ADHESIVE JOINT SHEAR STRENGTH

Three selected organofunctional silanes were employed in this study. Since these coupling agents may act as a bridge to bond the metal to the resin with a chain of primary bonds, a stronger interfacial bond could be expected.

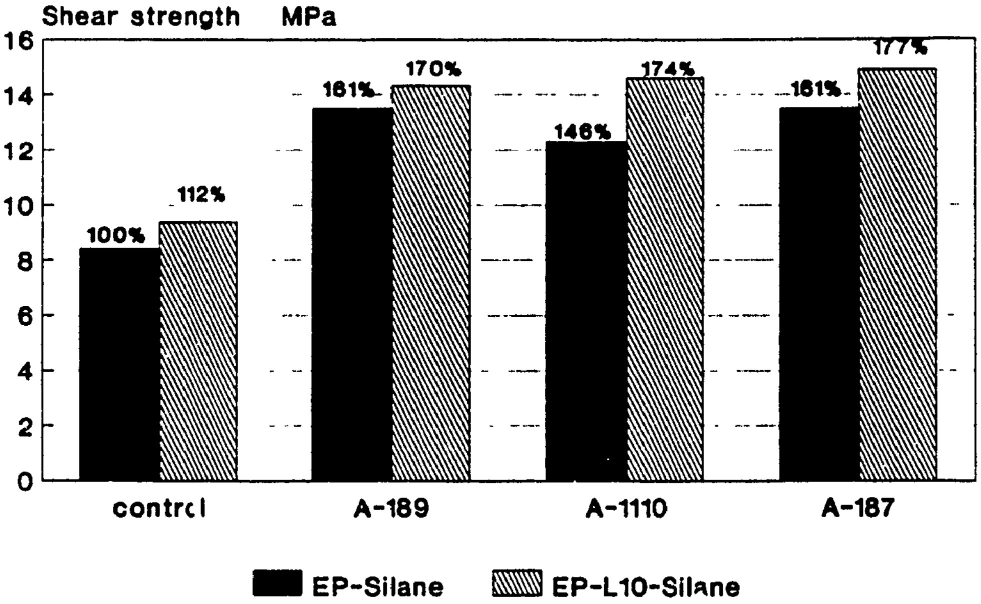
The effect of silanes on EP and EP-L10 was examined and is presented in Fig.6.2. The adhesive shear strength of the adhesive/aluminum joint was increased by introducing silane A-187, A-189, or A-1110 (2% by weight), respectively.

As can be seen from Fig.6.2, the strength of EP is increased to 112% by blending with lignin (10% of blend), and the strength of EP-L10 is increased to 170%, 174%, and 177% by introducing silane A-189, A-1110, or A-187 (2% of blend) respectively.

Several factors are thought to be involved in the mechanism of adhesive strength improvement for EP-L-silane/aluminum joints.

First, the improvement of adhesive strength is attributed to the interfacial Si-O-Metal bonds which might be

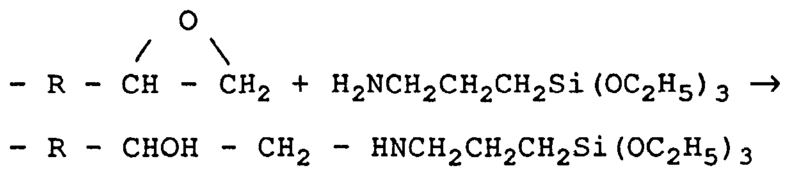
Fig.6.2 Effect of silanes on adhesive joint shear strength of EP and EP-L10[3]



EP: GY6010-TETA
L10: Tomlinite lignin,10%

formed on the interface of silane to metal [189].

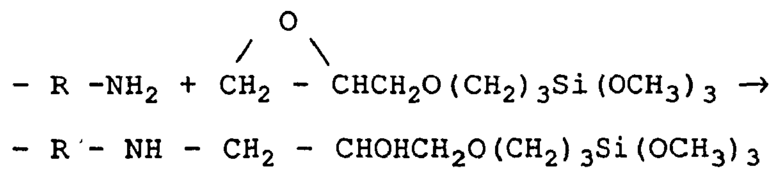
Second, it seems that chemical bonds are formed between the silane and the resin according to the chemical bonding theory of the coupling agent [189]. In the system studied, for example, the possible chemical reaction between aminoalksilane A-1110 and EP in the EP-L network is as follows [190]:



$$-R-\overset{O}{\overbrace{CH-CH_2}} + H_2NCH_2CH_2CH_2Si(OC_2H_5)_3 \rightarrow$$
$$-R-CHOH-CH_2-HNCH_2CH_2CH_2Si(OC_2H_5)_3$$

(1)

and the possible chemical reaction between silane A-187 and polyamine in the EP-L network is the following [190]:



$$-R-NH_2 + \overset{O}{\overbrace{CH_2-CH}}CH_2O(CH_2)_3Si(OCH_3)_3 \rightarrow$$
$$-R'-NH-CH_2-CHOHCH_2O(CH_2)_3Si(OCH_3)_3$$

(2)

Third, the results from Fig.6.2 also point out that the adhesive strength of EP-L10-silane is always higher than that of EP-silane as follows:

Relative strength			
EP-Silane		EP-L10-Silane	
EP	100%	EP-L10	112%
EP-A189	161%	EP-L10-A189	170%
EP-A1110	146%	EP-L10-A1110	174%
EP-A187	161%	EP-L10-A187	177%

This is partly due to the functional groups presented in lignin, such as hydroxyl (10.7% by weight), methoxyl (17.2% by weight) and carbonyl (5.0% by weight), which may bond with organofunctional silanes. For example, the possible reaction between aminoalkylsilane A-1110 and the carbonyl group of lignin in the EP-L network is as follows [190]:

$$-R_2CO + NH_2(CH_2)_3Si(OC_2H_5)_3 \rightarrow$$
$$-R_2C = N(CH_2)_3Si(OC_2H_5)_3 \quad + \quad H_2O \qquad (3)$$

6.4 WATER RESISTANCE

The durable adhesion of epoxy resin to metal in the presence of moisture has been shown to be difficult to achieve [191]. The strength of these systems is typically adequate for most structural applications. However, the deleterious effect of moisture on the bonding between the metal and the adhesive must be taken into account if epoxy resins are to be used for bonding metals in moist or humid environments. This places severe limitations on the number of structural bonding applications where epoxy adhesives could be used.

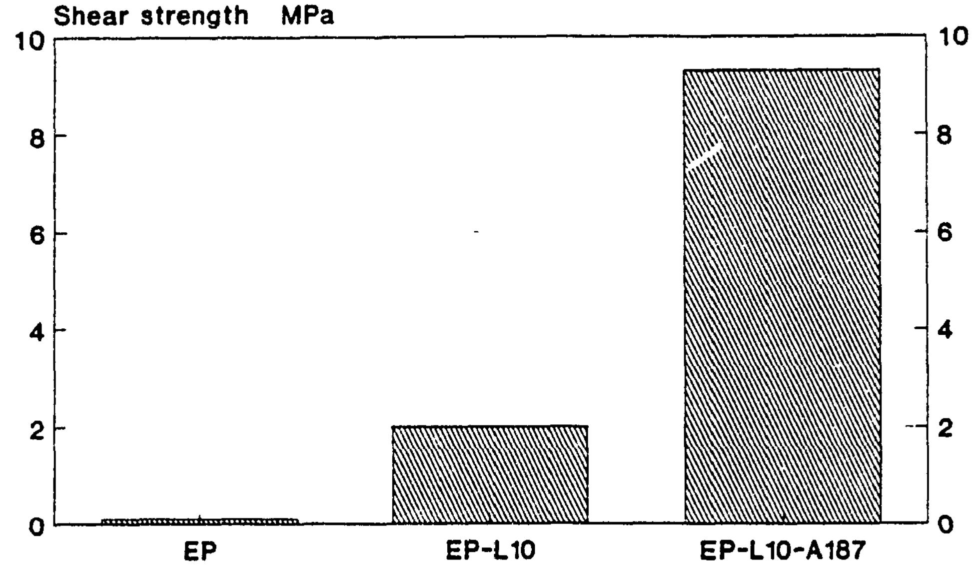
Several research groups have studied the effects of water on the durability of structural joints. Kerr, MacDonald, and Orman [192] in their study of epoxy adhesives exposed to saturated atmospheres of water found that hydrogen bonding interactions between the adhesive and metal were disrupted by the accumulation of water on the oxide surface. The water displaced the resin thereby greatly weakening the bond.

From the above discussion, it follows that it should be possible to improve the durability of bonded joints by the introduction of suitable coupling agents at the interface. If the coupling agent is capable of chemically interacting with the metal or its oxide, displacement of the adhesive by water at the interface will be prevented.

The silane coupling agent A-187 (2% of blend) was used to modify the EP and EP-L10 adhesives. The influence of silane A-187 on the adhesive joint shear strength of EP-A187/Aluminum and EP-L10-A187/Aluminum lap joint specimens, which were immersed in water at 23°C for 630 hours, is shown in Fig.6.3 and Fig.6.4. The adhesive joint shear strength was improved significantly by the introduction of silane A-187 as shown in Fig.6.3. The water resistance of EP-L10-A187 is much better than that of EP and EP-L10. Fig.6.4 gives the relative decrease in strength of EP, EP-L10 and EP-L10-A187 after immersion in water. The strength of EP fell to 1% of its control after immersion in water for 630 hours; the joints were almost in failure. The strength of EP-L10 fell to 21% of its control, while the strength of EP-L10-A187 fell to 62% of its control. Therefore, we may consider that the EP-L10-A187 shows superior durability.

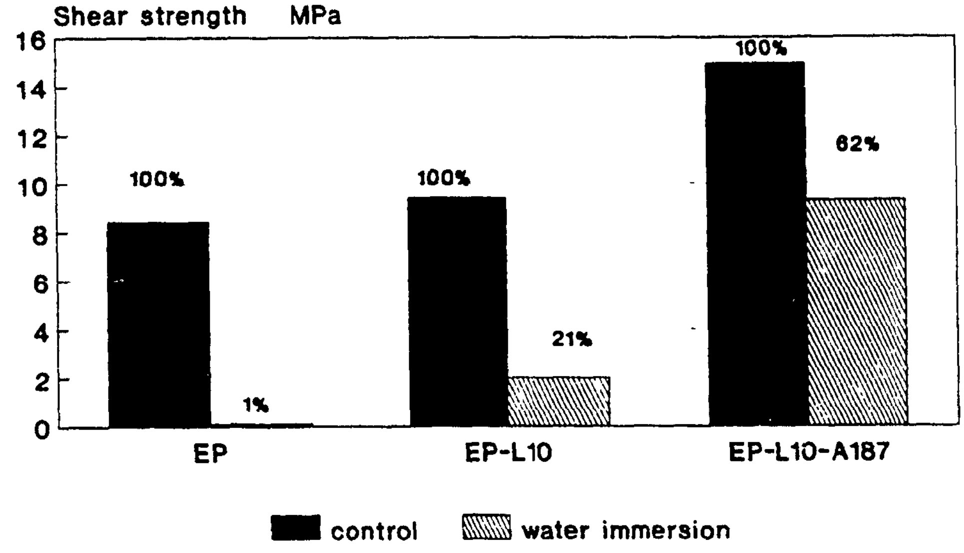
The significant improvement in bond durability confirms that organofunctional silanes may interact with both the metal surface and the EP-L adhesive system, resulting in a stronger link between the metal substrate and the adhesive.

Fig.6.3 Effect of Silane on Water Resistance of EP-L10 [3]
(Immersion in water at 23°C for 630 h)



EP: GY6010-TETA
L10: Tomlinite lignin, 10%
A187: Silane, 2%

Fig. 6.4 Water Resistance of EP, EP-L10
AND EP-L10-A187
(Immersion in water at 23° C for 630 h)



EP: GY6010-TETA
L10: Tomlinite lignin, 10%
A187: Silane, 2%

6.5 UV EXPOSURE

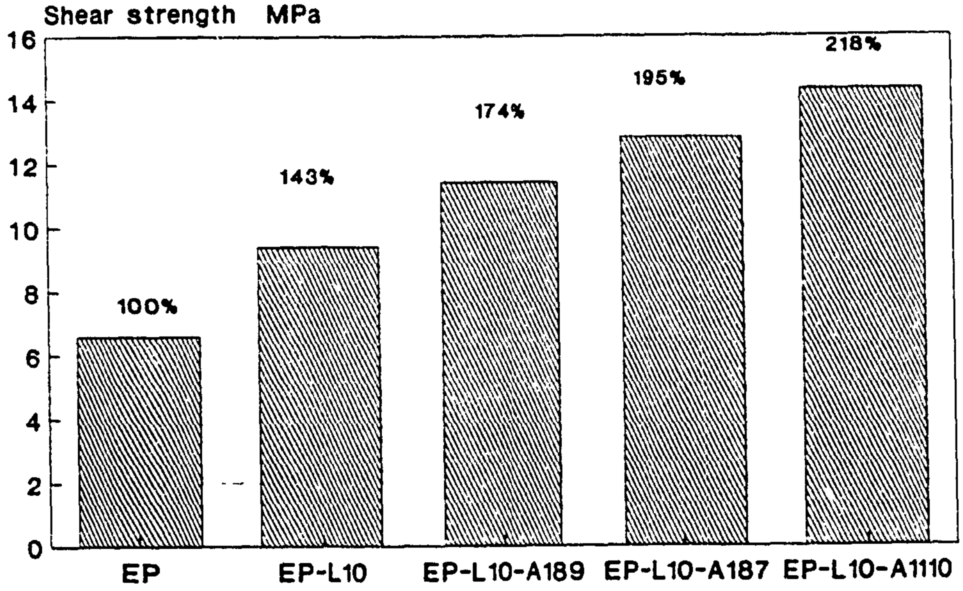
The organofunctional silane additives (2% of blend) also improve the photostability of EP and EP-L10 as shown in Fig.6.5. After 700 hours of UV exposure, the adhesive joint shear strength of EP-L10 is 143% of the control EP, while the adhesive strengths of EP-L10-Silane blends are 174%, 195% and 218% of the control EP respectively for the three different silanes.

As shown in Fig.6.6, the adhesive joint shear strength of EP-L10-Silane fell less than that of the control EP after UV exposure. Fig.6.6 also points out that the EP-L10 keeps the same adhesive strength before and after UV exposure. This may be attributed to the presence of lignin, which provides excellent weather durability [166].

6.6 SUMMARY

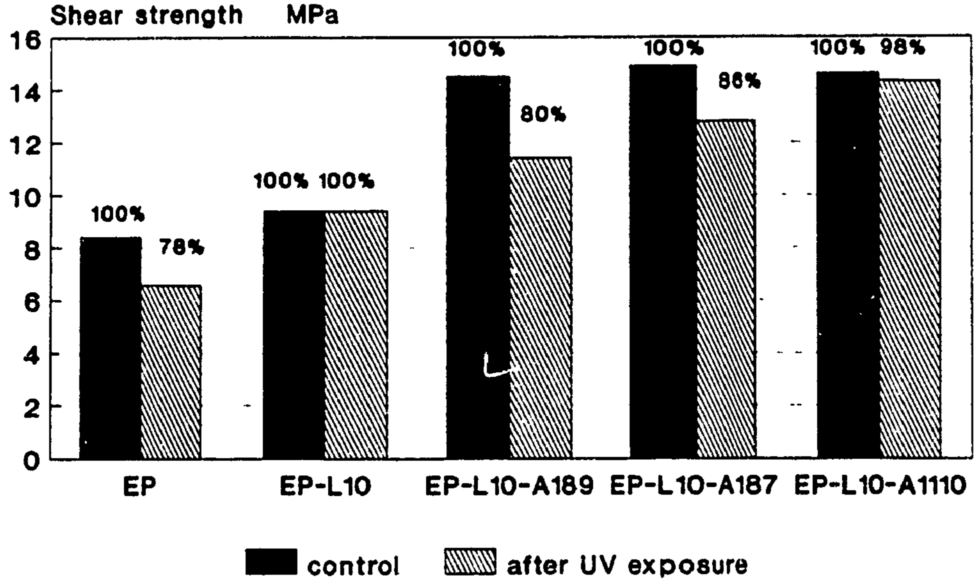
The organofunctional silane coupling agents were employed to modify the EP-L adhesive. The dual organic-inorganic functionality of the organofunctional silanes permits an improvement in bonding between the inorganic substrate and the organic EP-L adhesive. In this way, the adhesive joint shear strength and the durability of EP-L have been improved significantly by the introduction of silanes (2% of blend).

Fig.6.5 Effect of Silane on UV Resistance of EP-L10
(400 W lamp, 15 cm distance, 700 h)



EP: GY6010-TETA
L10: Tomlinite lignin, 10%

Fig.6.6 UV Resistance of EP, EP-L10 and EP-L10-Silane
(400 W lamp, 15 cm distance, 700 h)



EP: GY6010-TETA
L10: Tomlinite lignin, 10%

The adhesive joint shear strengths of EP, EP-L10 and EP-L10-Silane are as follows:

	ADHESIVE JOINT SHEAR STRENGTH	
	MPa	%
EP	8.4	100%
EP-L10	9.4	112%
EP-L10-A189	14.3	170%
EP-L10-A1110	14.6	174%
EP-L10-A187	14.9	177%

The adhesive joint shear strengths of EP, EP-L10 and EP-L10-Silane after immersion in water at 23°C for 630 hours are as follows:

	ADHESIVE JOINT SHEAR STRENGTH (MPa)
EP	0.1
EP-L10	2.0
EP-L10-A187	9.3

The adhesive joint shear strengths of EP, EP-L10 and EP-L10-Silane after UV exposure for 700 hours are as follows:

ADHESIVE JOINT SHEAR STRENGTH

	MPa	%
EP	6.57	100%
EP-L10	9.39	143%
EP-L10-A189	11.4	174%
EP-L10-A187	12.8	195%
EP-L10-A1110	14.3	218%

CHAPTER 7

POLYMER SURFACE AND ADHESION

7.1. INTRODUCTION

Analysis of the polymer surface is becoming increasingly important in general studies of adhesive bonding.

It has been recognised for many years that the establishment of thermodynamic surface parameters at the contact interface is a necessary, . though sometimes insufficient, requirement for developing a strong adhesive bond. Since EP-L is a novel adhesive, it is necessary to establish its surface parameters.

Adhesion refers to the state in which two dissimilar bodies are held together by intimate interfacial contact. The interfacial forces holding the two phases together may arise from Van der Waals forces, chemical bonding or electrostatic attraction. The mechanical strength of the system is determined not only by the interfacial forces, but also by the mechanical properties of the interfacial zone and the two bulk phases. Thermodynamic adhesion refers to equilibrium interfacial forces or energies associated with reversible processes, such as the work of adhesion. It is a hypothesis that it should be possible to correlate the measured strength of an adhesive joint with the thermodynamic work of adhesion

[189].

In this chapter, the contact angle studies of EP, EP-L10 and EP-L10-A187 are presented. The solid surface free energy is determined. Values of the work of adhesion, the interfacial free energy, and the interaction parameter are calculated from contact angle data at the adhesive/liquid interface and at the adhesive/metal substrate interface as a function of lignin and organo-silane additives. These thermodynamic parameters are compared with measured adhesive joint shear strength, and the relationships between them are discussed [3,5].

The contact angle was measured by a contact angle meter, which was equipped with a microscope and a video system. The microscope with a magnification of 10x is mounted on a cross-carriage so that it can be moved left or right and high or low relative to the stage on which the drop is placed. Measurements were carried out with distilled water and methylene iodide (Anachemia) at 23°C using the sessile drop method. The volume of the sessile drop was maintained as 5 μl in all cases using a micropipette. The contact angle was measured on the screen of a video system within 30-60 seconds of the addition of the liquid drop. Values used for plotting results were averages of 10 measurements with standard deviation of ± 2°.

7.2. POLYMER SURFACE BEHAVIOUR

7.2.1 THEORY AND CALCULATIONS

The classic equation relating the solid surface free energy (γ_s), the surface free energy of a liquid (γ_l), the interfacial free energy between the solid and the liquid (γ_{sl}), and the contact angle (θ) is the Young-Dupré equation [193].

$$\gamma_l \cos\theta = \gamma_s - \gamma_{sl} \tag{1}$$

A plot of cosθ against the surface tension for a homologous series of liquids, γ_l, can be extrapolated to give a critical surface tension, γ_c, at which $\cos\theta = 1$ [194]. γ_c has been taken as an approximate measure of the solid surface free energy (γ_s). A more appropriate method has been presented by Fowkes. He considered solid dispersion forces using a geometric mean equation [195]. Later, Owens and Wendt [196] and Kaelble [197] modified Fowkes' approach further by incorporating the polar attraction forces which include the hydrogen bonding forces. Wu [198,199] has found a much better agreement to obtain γ_s when he used a harmonic mean equation. In this equation, the "reciprocal-mean" polar term is based on empirical grounds. This appears to be accurately applicable to polymers, organic liquids and water systems [198]. Wu's approach has been satisfactorily used by several authors [200-206]. The harmonic mean equations were used in this present study. Water and methylene iodide which have been reported to be a useful pair of liquids of dissimilar polarity in Wu's approach [201].

Wu's equations for water and methylene iodide are written as

$$(1 + \cos\theta_w)\gamma_w = 4\left[\frac{\gamma_w^d \ \gamma_s^d}{\gamma_w^d + \gamma_s^d} + \frac{\gamma_w^p \ \gamma_s^p}{\gamma_w^p + \gamma_s^p}\right] \qquad \textbf{(2)}$$

and

$$(1 + \cos\theta_m)\gamma_m = 4\left[\frac{\gamma_m^d \ \gamma_s^d}{\gamma_m^d + \gamma_s^d} + \frac{\gamma_m^p \ \gamma_s^p}{\gamma_m^p + \gamma_s^p}\right] \qquad \textbf{(3)}$$

where $\gamma^d{}_w$ and $\gamma^p{}_w$ are the dispersion and polar components of the surface free energy of water (γ_w): γ_m^d and γ_m^p are the dispersion and polar components of surface free energy of methylene iodide (γ_m). Data for water and methylene iodide were taken from the literature [198,199]:

$$\begin{array}{lll} \gamma_w = 72.8mJ/m^2 & \gamma_w^d = 22.1mJ/m^2 & \gamma_w^p = 50.7mJ/m^2 \\ \gamma_m = 50.8mJ/m^2 & r_m^d = 44.1mJ/m^2 & \gamma_m^p = 6.7mJ/m^2 \end{array}$$

γ_s^d and γ_s^p for EP, EP-L10 and EP-L10-A187 were determined by solving equations (2) and (3).

The total solid surface free energy, γ_s, is given by [199]

$$\gamma_s = \gamma_s^d + \gamma_s^p \qquad \textbf{(4)}$$

The work of adhesion, W_a, between a solid and a liquid is given by [199]

$$W_a = (1+\cos\theta)\gamma_l \qquad (5)$$

where γ_l is the liquid free energy.

The interfacial free energy, γ_{sl}, is calculated from Dupré's equation [207]:

$$\gamma_{sl} = \gamma_s + \gamma_l - W_a \tag{6}$$

The spreading coefficient, S_c, is calculated from [208]

$$S_c = \gamma_l (\cos\theta - 1) \tag{7}$$

Girifalco-Good's interaction parameter, ϕ, between the polymer and the liquid, is calculated from the relation [209]

$$\phi = \frac{\gamma_l (1 + \cos\theta)}{2 (\gamma_s \cdot \gamma_l)^{1/2}} \tag{8}$$

7.2.2. RESULTS

The contact angle values are shown in Table 7.1. As can be seen, the wettability was improved by adding lignin and organosilane to epoxy polymer. EP-L10-A187 showed the highest wettability with both water and methylene iodide.

Data of the work of adhesion are also shown in Table 7.1. The EP-L10-A187 shows the highest work with both water and methylene iodide, while EP shows the lowest value. This indicates that the highest work is required to separate the EP-L10-A187 from both polar and non-polar liquids.

Table 7.1 Comparison of surface parameters of EP, EP-L10 and EP-L10-A187 [3]

		EP	EP-L10	EP-L10-A187
Contact angle (degree)	θ_w*	81	75	69
	θ_m**	50	38	18
Work of adhesion (mJ/m^2)	W_a (w)*	84.2	91.6	97.7
	W_a (m)**	83.5	90.8	99.1
Surface free energy (mJ/m^2)	γ_s	37.9	43.7	50.8
	$\gamma^d{}_s$	26.9	31.6	37.8
	$\gamma^p{}_s$	11.0	12.1	13.0
Interfacial free energy (mJ/m^2)	γ_{sl} (w)*	26.5	24.9	24.7
	γ_{sl} (m)**	5.2	3.7	2.5
Spreading coefficient (mJ/m^2)	S_c (w)*	-61.4	-54.0	-46.7
	S_c (m)**	-18.1	-10.8	-2.5
Interaction parameter	ϕ (w)*	0.801	0.812	0.813
	ϕ (m)**	0.951	0.964	0.976

* to water
** to methylene iodide

The polymer solid surface free energy, γ_s, obtained from equations (2), (3) and (4) based on the contact angle values of water and methylene iodide shows the highest value for EP-L10-A187 and the lowest for EP (Table 7.1).

The values of γ_s^d and γ_s^p are also shown in Table 7.1. As can be seen, EP-L10 has higher dispersion and slightly higher polar components than EP. When EP-L10 is blended with silane, γ_s^d and γ_s^p show further increases.

Due to the introduction of silane, the glass transition temperature of the blend decreases responding to the increase in mobility and plasticity of macromolecules. As K.T. Varughese [205] suggested, the increase in mobility may be the possible reason for the increase in γ_s^d. The hydrolysable groups of silane may raise the γ_s^p of the blend [199].

Table 7.1 also presents the interfacial free energy (γ_{sl}) between the polymer surface and the liquids. The γ_{sl} values for the interface between EP-L10-A187 and both liquids are lower than those for EP-L10. However, the values for EP-L10 are lower than those for EP. In general, the lower the value of γ_{sl}, the higher the work of adhesion (as shown in equation (6)) and the higher the wettability [205,210]. Thus, the γ_{sl} values are in accordance with the other mentioned parameters.

The spreading coefficient, S_c, is the ability of a drop of liquid to spread over a solid [208]. A liquid will spontaneously wet and spread on a solid surface if S_c is positive. A negative S_c implies lack of wetting and spreading and thus, the existence of a finite contact angle (i.e. $\theta > 0$). The less negative S_c indicates a better wettability. As shown in Table 7.1, the EP-L10-A187 has less negative S_c values with both water and methylene iodide than EP-L10, indicating higher wettability, whereas EP shows more negative S_c values than EP-L10, indicating lower wettability.

In order to obtain an understanding of the degree of interaction between the test liquids and the polymer surface, Girifalco-Good's interaction parameter was calculated using equation (8), the results of which are presented in Table 7.1. For interaction parameter values in order of highest to lowest for both water and methylene iodide, the materials rank as follows:

EP-L10-A187 > EP-L10 > EP

The highest value obtained in the case of EP-L10-A187/liquid indicates that the greatest interaction occurs between EP-L10-A187 and liquids.

7.3. RELATIONSHIPS BETWEEN CALCULATED WORK OF ADHESION AND EXPERIMENTAL ADHESIVE JOINT SHEAR STRENGTH

7.3.1. THEORY AND CALCULATIONS

Wu's approach can also be used to calculate the thermodynamic work of adhesion between a solid adhesive and a metal substrate [199,206,211].

The work of adhesion is given by

$$W_a = 4\left[\frac{\gamma_1^d \cdot \gamma_2^d}{\gamma_1^d + \gamma_2^d} + \frac{\gamma_1^p \cdot \gamma_2^p}{\gamma_1^p + \gamma_2^p}\right] \tag{9}$$

where γ_1^d and γ_1^p are the dispersion and polar components of the surface free energy for solid adhesive, and γ_2^d and γ_2^p are those for the metallic substrate. In this study, pretreated aluminum substrates (abraded with No.100 emery cloth and then degreased with acetone) were used. The contact angle measurements were carried out on the pretreated surface in the same way as on polymer blends and the surface free energy was found to be γ_2 = 55.5 mJ/m^2, and γ_2^d = 36.0 mJ/m^2, γ_2^p = 19.5 mJ/m^2.

In the presence of water, the work of adhesion, W_{al}, is calculated according to the following relation [199,206,211]:

$$W_{al} = 2\gamma_w + 4\left[-\frac{\gamma_1^d \cdot \gamma_w^d}{\gamma_1^d + \gamma_w^d} - \frac{\gamma_2^d \cdot \gamma_w^d}{\gamma_2^d + \gamma_w^d} - \frac{\gamma_1^p \cdot \gamma_w^p}{\gamma_1^p + \gamma_w^p} - \frac{\gamma_2^p \cdot \gamma_w^p}{\gamma_2^p + \gamma_w^p} + \frac{\gamma_1^d \cdot \gamma_2^d}{\gamma_1^d + \gamma_2^d} + \frac{\gamma_1^p \cdot \gamma_2^p}{\gamma_1^p + \gamma_2^p}\right] \tag{10}$$

Different studies have attempted to correlate the experimental results of adhesive joint strengths with the theoretical work of adhesion [210,212-215]. Since other contributing factors often overshadow adhesive joint strength, a good correlation sometimes does not exist. However, the general trends predicted by W_a have sometimes been found to hold true for experimentally measured systems. At least for certain adhesion systems, the work of adhesion may have underlying control over the observed joint strength.

In addition to the work of adhesion, two other thermodynamic parameters, namely interfacial free energy and Girifalco-Good's interaction parameter, can also be useful in explaining observed adhesion phenomena [210,216].

The interfacial free energy, γ_{12}, is calculated from equation (6) as mentioned above.

The interaction parameter, ϕ, is calculated from [208]

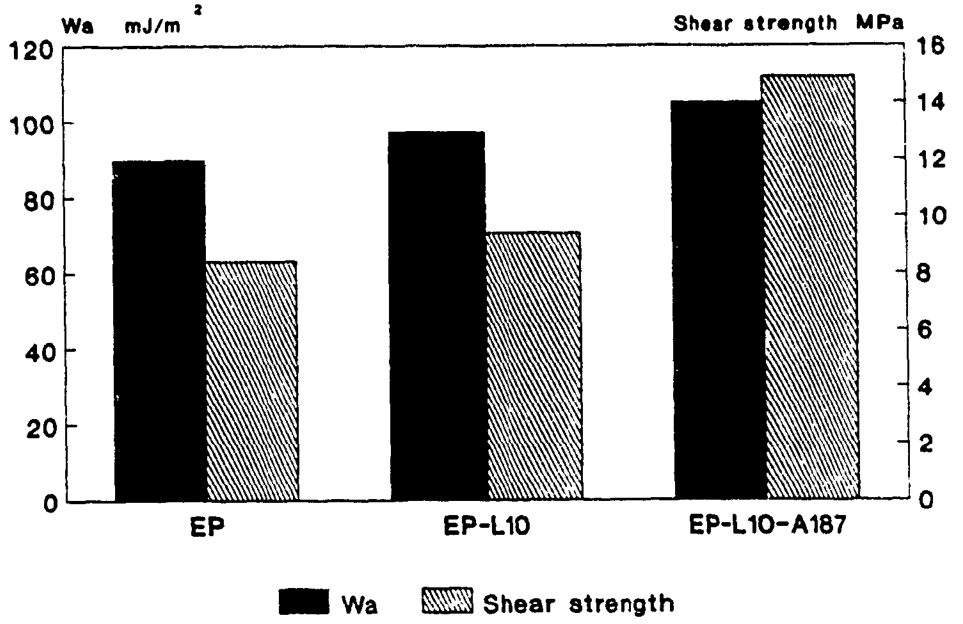
$$\phi = \frac{\gamma_1 + \gamma_2 - \gamma_{12}}{2\,(\gamma_1 \cdot \gamma_2)^{\frac{1}{2}}} \qquad \textbf{(11)}$$

where γ_1 is the adhesive system surface free energy and γ_2 is the metallic adherent surface energy.

7.3.2. RESULTS

Equation (9) was used to calculate the value for the work of adhesion between the adhesive and aluminum, which is the work required to separate the adhesive from the aluminum substrate. The results are shown in Fig.7.1. The EP modified with lignin has increased the work of adhesion at the EP-L10/aluminum interface. The EP-L10 modified with silane has even further increased W_a. In the shear strength test, failure occurred at the adhesive/aluminum interface which can be clearly observed by microscope, therefore it is possible to correlate the adhesive joint shear strength with the calculated thermodynamic work of adhesion. A comparison of

Fig.7.1 Calculated work of adhesion compared with adhesive joint shear strength [3]



the calculated work of adhesion and the measured adhesive joint shear strength values (Fig.7.1) shows that both exhibit the same increasing trend as the epoxy is blended with lignin and increase further at the EP-L10-A187/aluminum interface, suggesting a possible correlation between them.

Interfacial free energy is calculated by equation (6) for the adhesive/aluminum interface. The results (Fig.7.2) show that γ_{12} for EP/aluminum is higher than that for EP-L10/aluminum. However, the latter is higher than that for EP-L10-A187/aluminum. Mittal [210] has found that, in general, the lower the value of γ_{12}, the higher the adhesive joint strength. Thus, the interfacial free energy behaviour is also in accordance with the behaviour of the observed adhesive joint shear strength (Fig.7.2). Mittal [210] has proposed γ_{12} as the most important criterion when optimizing adhesive joint strength.

Girifalco-Good's interaction parameter (ϕ) between the adhesive and the aluminum substrate is calculated using equation (11). The values are given in Fig.7.3. These results are also in agreement with the shear strength results. Compared with EP, EP-L10 has a higher interaction parameter partly due to the considerable number of functional groups in lignin (i.e. hydroxyl, methoxyl, carbonyl and so on). The EP-L10-A187 has the highest ϕ value due to the introduction of silane which is able to bond with the metallic substrate.

Fig.7.2 Interfacial free energy compared with adhesive joint shear strength [3]

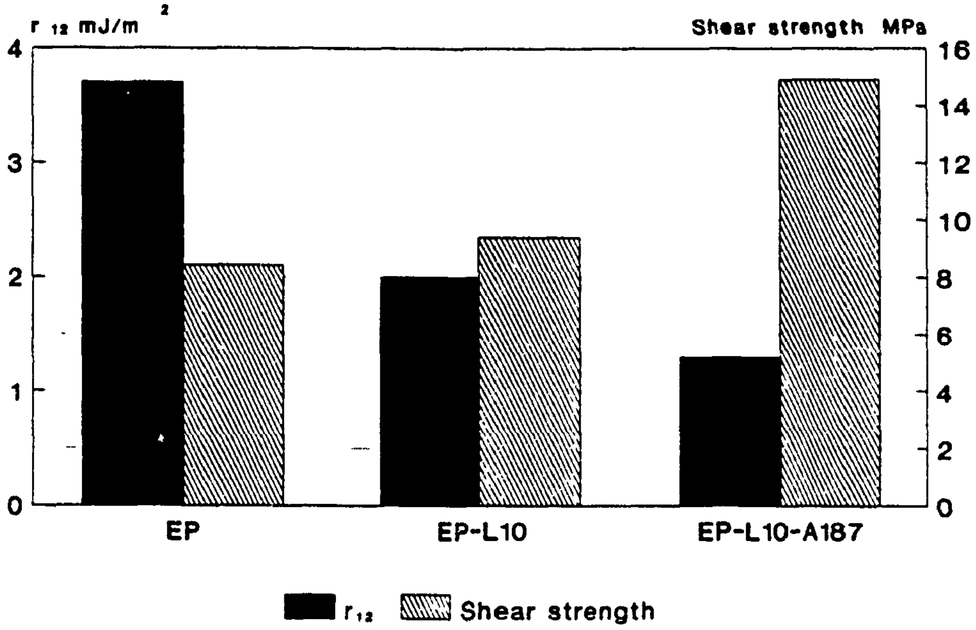
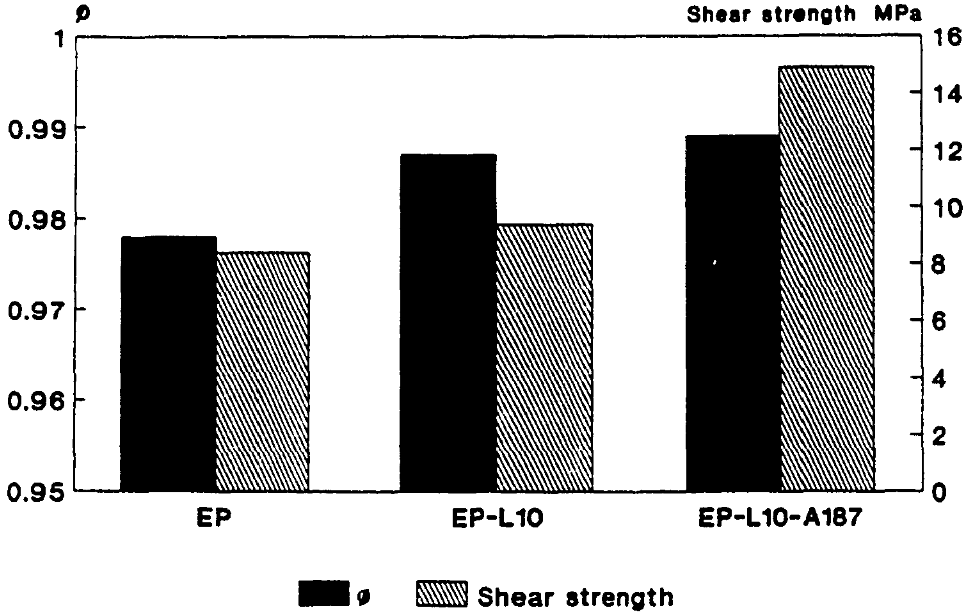


Fig.7.3 Interaction parameter (adhesive/Al) compared with adhesive joint shear strength [3]



The work of adhesion for adhesive/aluminum in the presence of water is calculated from equation (10). The results as given in Table 7.2 shows that the W_{al} for EP-L10-A187 is higher than that for EP-L10, and the latter is higher than W_{al} for EP. Likewise, the adhesive shear strength of the adhesive/aluminum joint after immersion in water (Table 7.2) exhibits a similar trend, suggesting a possible correlation between them.

From all the surface parameters and adhesive joint shear strength data discussed above, it seems that there is a direct correlation between the wetting, adhesion and adhesive strength of EP, EP-L10 and EP-L10-A187. The wetting, work of adhesion and other surface thermodynamic parameters exhibit similar behaviour to the observed adhesive joint shear strength. Wetting may affect adhesion in two ways. First, incomplete wetting will produce interfacial defects and thereby lower adhesive bond strength. Second, better wetting can increase the adhesive joint strength by increasing the work of adhesion, which may be proportional to the fracture energy [199]. Another explanation for the increase in adhesive strength with decrease in contact angle is attributed to the fact that a small contact angle will reduce the stress concentration at the edge of the flaws where the adhesive has failed to completely wet the adherent [217].

Table 7.2 Calculated W_{a1} compared with adhesive joint shear strength in water* [3]

	EP	EP-L10	EP-L10-A187
W_{a1} (mJ/m^2)	35.9	37.2	39.2
Adhesive Joint shear strength (MPa)	0.1	2.1	9.3

* Immersion in water (23°) for 630 h.

7.4. SUMMARY

Analysis of the polymer surface is becoming increasingly important in general studies of adhesive bonding. Since EP-L is a novel adhesive, it is necessary to establish its surface parameters.

Surface thermodynamic parameters, θ, γ_s, $\gamma^d{}_s$, $\gamma^p{}_s$, W_a, γ_{sl}, S_c and ϕ were determined for EP, EP-L10 and EP-L10-A187 using water and methylene iodide as test liquids. W_a, W_{al}, γ_{12}, and ϕ between these adhesives and the aluminum substrate were also established.

The wetting and thermodynamic work of adhesion at the adhesive/substrate interface show the following order: EP-L10-A187 > EP-L10 > EP, and the observed adhesive joint shear strength shows the same trend, suggesting a direct correlation between the established surface thermodynamic parameters and the observed adhesive strength.

CHAPTER 8

EFFECTS OF VARIOUS COMPONENTS ON ADHESIVE PROPERTIES, AND THE DURABILITY OF EP-L ADHESIVES

8.1 INTRODUCTION

Epoxy is a widely used polymeric material. Modern technology has led to the development of many types of epoxy-based adhesive systems. Epoxy-based adhesives have been formulated to meet various specifications and use criteria.

Lignin from different plants may differ one from the other and the lignin products from different technical processes are also different.

The studies in previous chapters are based on a few particular EP-L systems. In this chapter, the study is extended to various lignins, EP prepolymers, hardeners and other additives [6].

Lignins of different sources and techniques of isolation as well as lignin fractions having different molecular weights were blended in the EP systems.

The adhesive properties of EP-L polyblends are discussed when the EP prepolymer is an unmodified or modified DGEBA with reactive or non reactive diluents, and the hardener is a modified or unmodified aliphatic polyamine.

The incorporation of ordinary EP fillers in EP-L polyblends and the influence of a third polymeric component on the EP-L adhesive properties are discussed.

The durability of EP-L adhesives by accelerated weathering and UV exposure methods is also established in this chapter.

The polyblends were prepared by the same procedures as described in chapter 6. A filler or a third polymeric component was added at the same time as the lignin. The curing conditions and shear strength test procedures were the same as described in chapter 6.

8.2 COMPONENTS

8.2.1. EPOXY PREPOLYMERS AND HARDENERS

The EP prepolymers and the hardeners are commercial liquid products supplied by Ciba-Geigy Canada Ltd. The characteristics of the EP prepolymers and the hardeners are shown in Table 8.1 and 8.2. All data were furnished by the supplier.

8.2.2. LIGNINS

The EP-L polyblends were prepared with various types of kraft processed lignins from hardwood, softwood and eucalyptus wood as well as a lignin separated from aspenwood by a steam explosion procedure. Their physical characteristics are shown in Table 8.3.

Table 8.1
Characteristics of the Epoxy Prepolymers [6]

RESIN	BASIC COMPONENTS	EQUIVALENT WEIGHT (g/equiv)
CA 1200 resin	Diglycidyl ether of Bisphenol A (DGEBA) Neopentyl glycidyl diglycidyl ether	173-184
Araldite AY 103	DGEBA Di-n-butyl phthalate p-Tertiary butylphenyl glycidyl ether	225-238
Araldite GY 6010	Unmodified DGEBA	182-192

TABLE 8.2
Characteristics Of The Hardeners [6]

HARDENER	BASIC COMPONENTS	EQUIVALENTS WEIGHT (g/equiv)
HY 2992	Accelerated aliphatic polyamine	55
HY 956	Propoxylated-triethlene-tetramine Triethylenetetramine	47
TETA	Triethylenetetramine	23

TABLE.8.3 PHYSICAL CHARACTERISTIC OF LIGNINS [6]

NAME	TYPE	SPECIFIC GRAVITY[5]	Mw[6]	Mn[6]	Mw/Mn	AVERAGE PARTICLE SIZE[7] (µm)
Tomlinite[1] (TO)	kraft lignin from hardwood	1.29	2785	648	4.3	16
Indulin AT[2] (AT)	kraft lignin from softwood	1.24	2479	573	4.3	8
Eucalin[3] (EU)	kraft lignin from eucaliptus wood	1.38	-	-	-	10.5
SEL[4]	steam exploded lignin from aspen wood	-	6752	985	6.9	-

1. Domtar Corporation, Cornwall, Ontario
2. Westvaco, Chemical Division, Charleston, S.C. USA
3. Empresa National de Celulosas, S.Q. Madrid, Spain
4. Forintek Canada Corp., Ottawa, Ontario
5. Determined according to ASTM D-153
6. Tomlinite - determined by GPC [37]
   Indulin AT - literature data [218]
   SEL - data furnished by Foritek
7. D.Feldman, M.Lacasse: unpublished data

Tomlinite(TO), a hardwood lignin, was fractionated in three fractions with different molecular weight distribution and the obtained fractions were subjected to polyblending with EP polymers. Lignin fractionation was done according to the following procedure [219-221]:

After water extraction and drying, 30 g of lignin was suspended in 500 ml methylene chloride. The suspension was stirred at room temperature for 24 h. The undissolved material was filtered off and washed repeatedly with methylene chloride until the filtrate was almost colourless. The material was carefully dried in a vacuum at room temperature and then suspended in 500 ml methanol. The suspension was stirred at room temperature for 24 h. The methanol insoluble material was filtered off and washed with methanol until the filtrate was colourless and subsequently dried in a vacuum at room temperature.

The soluble fractions in methylene chloride and methanol were separated by evaporating the solvent under reduced pressure in a rotary evaporation system and then were dried in a vacuum at room temperature.

Molecular weight distributions were estimated by GPC using an acetylated form of lignin. Gel permeation chromatography was performed using a set of three columns consisting of crosslinked styrene divinylbenzene polymer (ultrastyragel 500 A in one column and ultrastyragel linear in two columns). The columns were connected to a Universal

Injector (Waters U6K) and an HPLC Pump (Water 510), and an R.I. Detector (Waters 410) were used. Tetrahydrofuran (THF) (Omnisolv BDH, suitable for chromatography) was used as the eluant at a flow rate of 1 ml/min; 100 μl injections of 0.2% acetylated lignin solutions in THF were made. The column calibration for molecular weight determination was made with a set of 10 polystyrene standards (Waters). Molecular weight averages (Mn and Mw) and polydispersity (Mw/Mn) were calculated from the retention times via a calibration curve using a computer (Waters 840 Control and Data Station) and Waters Expert GPC Software.

The molecular weight distributions of the unfractionated lignin and of its three fractions as obtained by GPC are shown in Fig.8.1. The number average (Mn) and weight average (Mw) molecular weights, calculated from the GPC curves (relative values related to polystyrene), polydispersity (Mw/Mn) and fractionation yields are listed in Table 8.4.

8.2.3. FILLERS

The EP-L polyblends were compounded with the following fillers:

(1) 1202 mineral aggregate (fine powder), the basic component of which is silica;

(2) Silica crystalline (fine powder) from Malvern Minerals Co.;

(3) Aluminum metal (fine powder) from Fisher Co.

FIG.8.1 THE MOLECULAR WEIGHT DISTRIBUTION OF TOMLINITE LIGNIN AND OF ITS FRACTIONS [6]

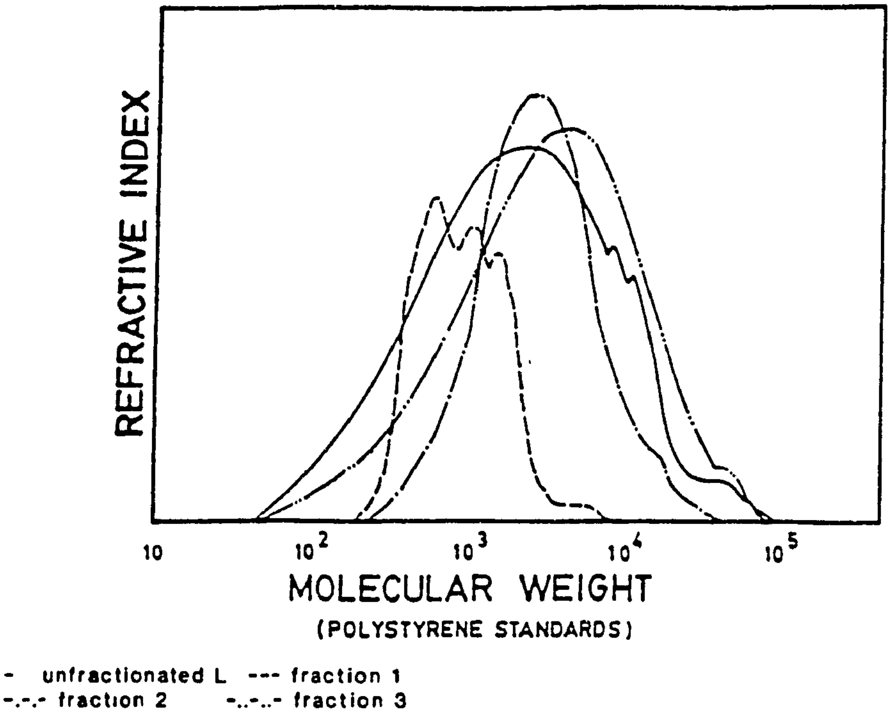


Table 8.4

Fractionation Yields, Average Molecular Weights And Polydispersity Of Tomlinite Lignin And Its Fractions [6]

FRACTION*	YIELD♦ %	Mn	Mw	Mw/Mn
1	27	405	690	1.7
2	30	698	1596	2.3
3	43	1080	5566	5.13
TOMLINITE		648	2785	4.2

♦ % of unfractionated lignin by weight

* Fraction 1: soluble in methylene chloride
Fraction 2: soluble in methanol
Fraction 3: insoluble fraction

8.2.4. THIRD POLYMERIC COMPONENTS

A commercial PVC (Geon resin) from B.F. Goodrich and Phenoxy resin from Aldrich Chemical Company were selected to separately modify EP-L.

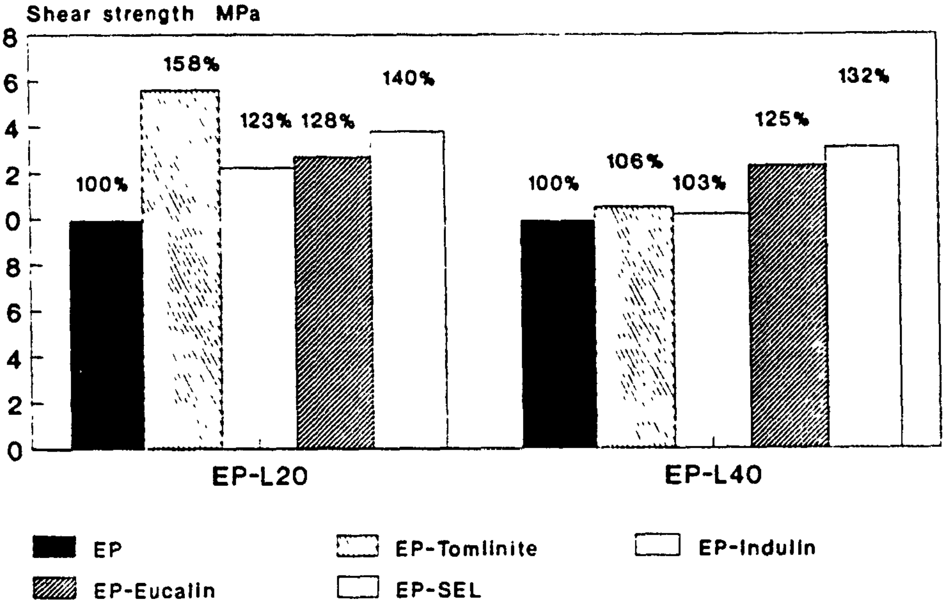
8.3. INFLUENCE OF VARIOUS TYPES OF LIGNIN

Lignin has a heterogeneous branched network of phenylpropane units. Its properties and composition are complex and they depend on the source and technique of isolation.

It is intended to establish if the source of lignin as well as its isolation technique could influence the adhesive behaviour of EP-L polyblends. Four different lignins, enumerated in Table 8.3, were blended with the same EP-hardener system (GY6010-HY956).

The values of adhesive joint shear strength for the formulations with different lignins which underwent the same curing conditions (100°C for 1 h) are shown in Fig.8.2. For the same amount of 20% lignin by weight (i.e. EP-L20), EP blended with Tomlinite lignin shows the highest joint shear strength (158% of the control EP), followed by the blend of EP with steam exploded lignin (140% of the control EP). The blend of EP with Eucalin lignin shows 128% and the blend of EP with Indulin lignin shows 123% of the control EP. Even at a 40% lignin by weight in polyblends (EP-L40), the adhesive

FIG.8.2 INFLUENCE OF DIFFERENT LIGNINS ON ADHESIVE JOINT SHEAR STRENGTH OF EP-L [6]



EP: GY6010-HY956

properties of the EP-L polyblends are still superior to the control EP and in this case the blend of EP with steam exploded lignin exhibits the highest improvement (132% of the control EP).

It appears likely that hardwood lignins (Tomlinite, Eucalin, steam exploded lignin), kraft processed or isolated by steam explosion, impart a better adhesivity to EP-L polyblends than softwood lignin (Indulin).

These results also indicate that although various types of lignin may have different influence on EP-L adhesive properties, a wide variety of lignins may be employed in EP-L polyblends with an improvement of adhesive joint shear strength. This is a greatly significant factor for utilization of various lignins.

8.4. INFLUENCE OF LIGNIN MOLECULAR WEIGHT

In order to establish the effect of molecular weight of lignin on EP-L adhesive properties, Tomlinite lignin was fractionated into three fractions with different average molecular weights. These three fractions as well as the unfractionated lignin were separately blended with the same EP system (GY6010-TETA).

According to the data presented in Table 8.4, all three lignin fractions have different Mw. Fraction 1 consists of lower Mw lignin with a narrow polydispersity (Mw/Mn = 1.7) while fraction 3 consists of a higher Mw lignin with a higher polydispersity (Mw/Mn = 5.13).

For the same amount of 10% lignin loading in EP-L polyblends (EP-L10), the adhesivity appears to correlate well with the Mw of each lignin fraction as shown in Fig.8.3. However, comparing the adhesive joint shear strength data of the polyblend with unfractionated lignin (Mw = 2875, Mw/Mn = 4.2) to that of the polyblend with fraction 2 (Mw=1596, Mw/Mn = 2.3), it appears likely that a higher degree of polydispersity of the unfractionated lignin has a detrimental effect on adhesivity even at a quite superior Mw. The fact that there is a very low adhesive joint shear strength value of the blend with fraction 1 (Mw = 690, Mw/Mn = 1.7) suggests that the detrimental effect results from the low molecular weight components present in unfractionated lignin.

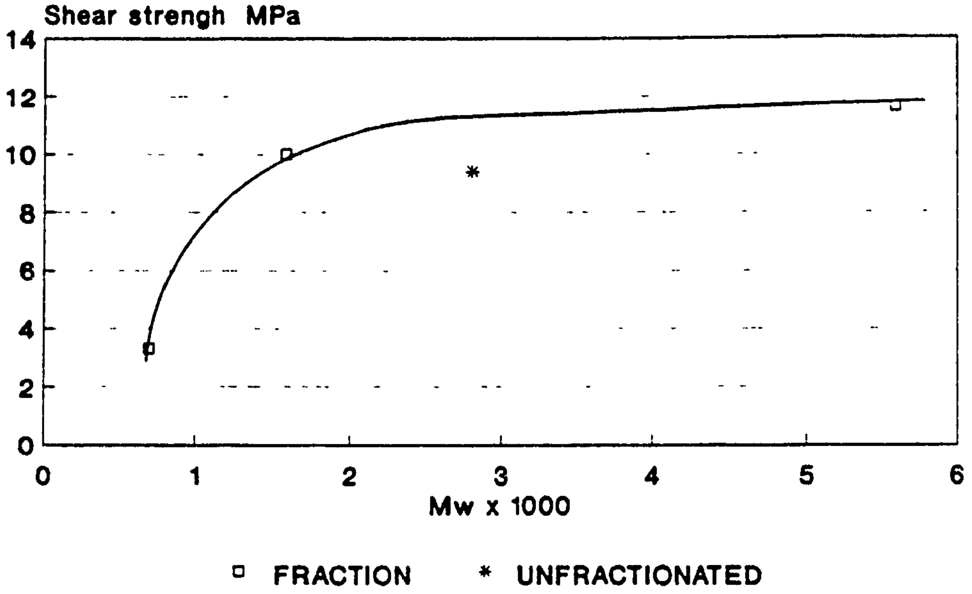
8.5. INFLUENCE OF VARIOUS TYPES OF EPOXY SYSTEMS

Tomlinite lignin was blended with three different EP systems which are basically of DGEBA type with or without diluents:

(1) CA 1200 epoxy with HY 2992 hardener, where the EP prepolymer is modified with a reactive diluent;

(2) Araldite AY 103 epoxy with HY 2992 hardener, where the EP prepolymer is modified with a reactive diluent and a non-reactive modifier;

FIG.8.3 RELATION BETWEEN Mw OF LIGNIN
AND THE ADHESIVE JOINT SHEAR
STRENGTH OF EP-L10 [6]



EP:GY6010-TETA
LIGNIN:TOMLINITE

(3) Araldite GY 6010 with HY 956 where the EP prepolymer is unmodified.

Their adhesive joint shear strength values of single-lap joints with aluminum substrate are shown in Fig.8.4.

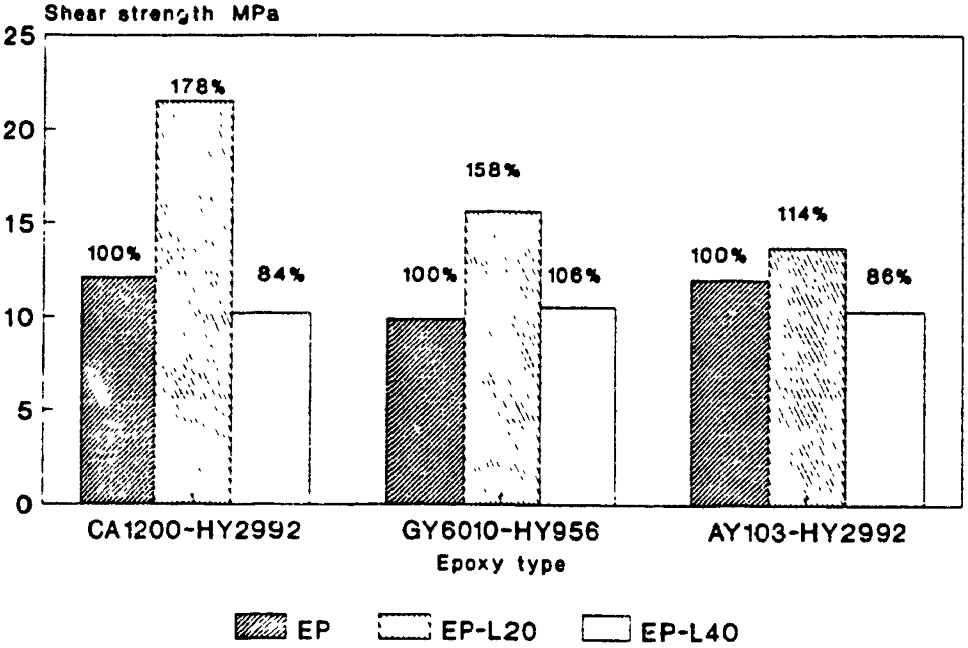
For the adhesive CA 1200, the adhesive joint shear strength was improved significantly by blending with lignin up to 20% by weight. As seen from Fig.4, the adhesive joint shear strength of EP-L20 is 178% of that of the control EP while the shear strength of EP-L40 is only 84% of the control EP.

The unmodified DGEBA EP, GY 6010, shows also a significant improvement of the adhesive joint shear strength by blending with lignin. For EP-L20, the shear strength is 158% of that of the control EP. The shear strength of EP-L40 is still 6% higher than that of the control EP.

In the case of polyblend with AY103, EP-L20 had only a small improvement of its adhesive joint shear strength (114% of the control EP). For EP-L40, its shear strength is only 86% of that of the control EP.

These results indicate that both epoxy systems with or without diluent and modifier can be blended with lignin resulting in an improvement of their adhesive joint shear strength in comparison with control EP. However, the improvement may vary for different epoxy systems.

FIG.8.4 INFLUENCE OF DIFFERENT EP ON ADHESIVE JOINT SHEAR STRENGTH OF EP-L[6]



Lignin: Tomlinite

8.6. INFLUENCE OF DIFFERENT HARDENERS

Various hardeners have different effects on the final properties of EP adhesives, even those that belong to the same class.

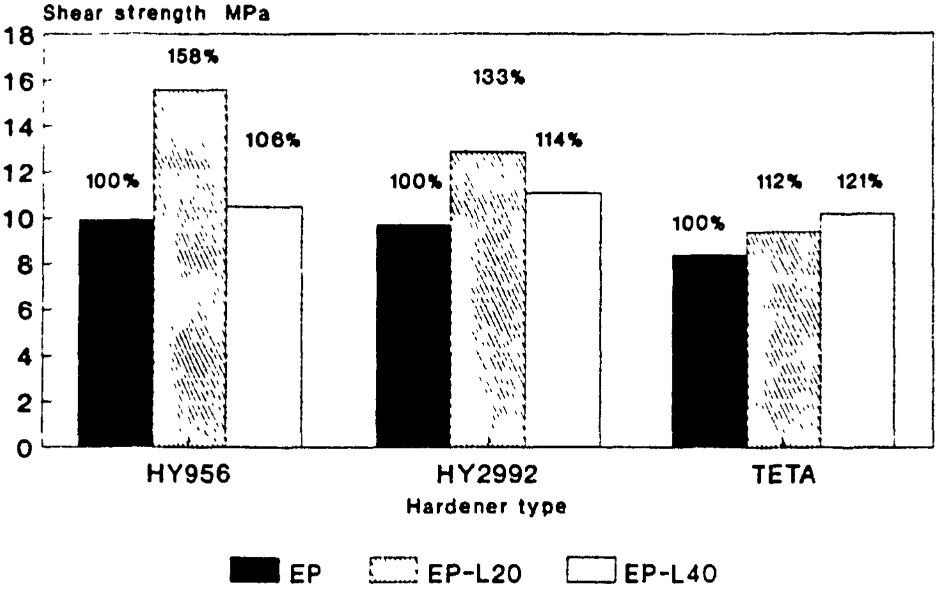
Three different hardeners from the class of aliphatic polyamine were evaluated in order to establish the influence on the adhesive properties of EP-L polyblends.

Three hardeners (see Table 8.2) were selected for the unmodified Araldite GY 6010 EP. All three formulations were prepared at the stoichiometric mixing ratio between EP and a hardener with the same lignin (Tomlinite, 20% or 40% of the blend by weight) and under the same curing conditions (100°C for 1 h). The results of the adhesive joint shear strength for all the formulations are shown in Fig.8.5. Hardener HY 956 seems to give the highest bond strength to EP-L20, followed by the HY 2992; the TETA gives the lowest adhesivity.

It is important to note that all of the three formulations containing up to 40% lignin show higher adhesive joint shear strength than the control EP.

These results depict that various polyamine hardeners can be employed in the curing process of the polyblends.

FIG.8.5 INFLUENCE OF DIFFERENT HARDENERS
ON ADHESIVE JOINT SHEAR STRENGTH
OF EP-L [6]



Epoxy GY6010
Lignin Tomlinite

8.7. MINERAL FILLERS IN EP-L ADHESIVES

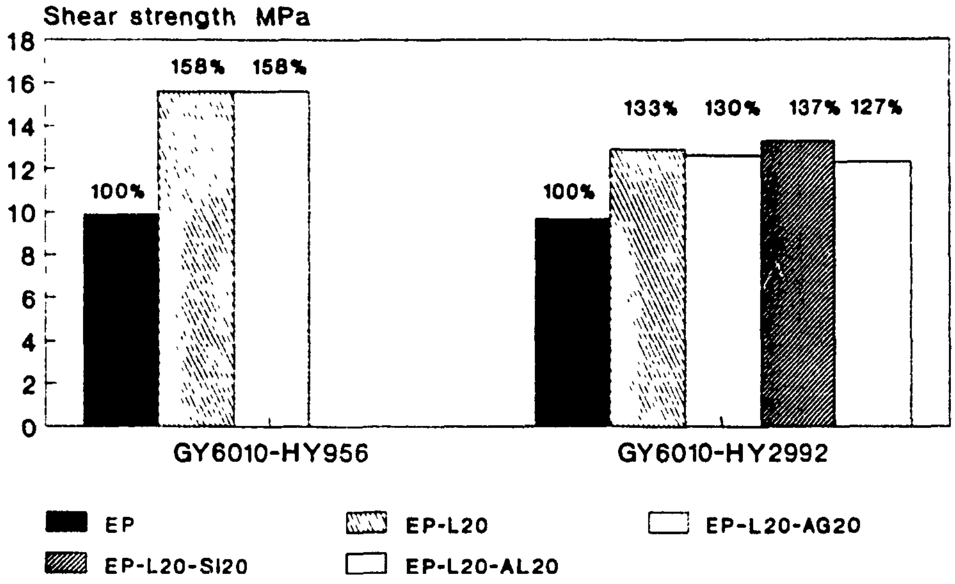
Mineral fillers are usually added to EP adhesives to serve a variety of functions and decrease their cost.

Three commercial fillers, 1202 aggregate, silica and aluminum (fine powder), have been separately added to the EP-L20 formulations (20% by weight).

The adhesive joint shear strength data for those filled polyblends are shown in Fig.8.6. The formulations of GY6010-HY2992-L20, to which were separately added the three different mineral fillers (20%), exhibit a similar adhesive joint shear strength to the EP-L20 without filler. In the case of the GY6010-HY959-L20 formulation, the additional 20% aggregate provides to EP-L20 the same adhesive joint shear strength as the EP-L20 without filler, i.e. 158% of the control EP.

It seems that the EP-L formulations tolerate different mineral fillers (20% by weight) without a detrimental influence on their adhesive joint shear strength. In order to obtain some specific functions like reinforcement and thermal stability and to decrease the cost of adhesives, mineral fillers can be selected for such EP-L formulations.

FIG.8.6 INFLUENCE OF FILLERS ON ADHESIVE JOINT SHEAR STRENGTH OF EP-L20 [6]



AG20:Aggregate 20%
SI20:Silica 20%
AL20:Aluminum 20% Lignin:Tomlinite

8.8.THIRD POLYMERIC COMPONENT IN EP-L ADHESIVES

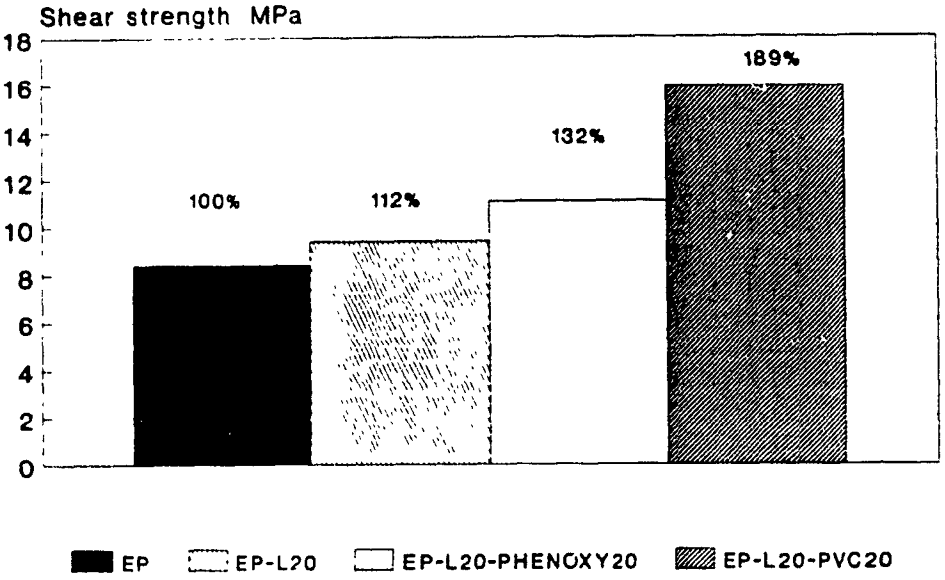
The efforts to modify EP-L polyblend properties involve the addition of a third macromolecular component. Polyvinyl chloride (PVC) and Phenoxy resin were used to modify EP-L resin.

PVC can be easily blended with a variety of other polymers in order to obtain new compounds with specific characteristics.

The PVC powder (20% of blend by weight) was added to the GY 6010 EP at the same time as Tomlinite lignin, and the mixture was stirred for two minutes at room temperature. After mixing with TETA hardener, single-lap aluminum specimens were prepared. The shear strength test was carried out after the specimens were cured for 1 h at 150°C. The results (Fig.8.7) show significant improvement of adhesive joint shear strength which is higher than EP-L20 polyblend without PVC and 189% of the control EP.

A Phenoxy resin was also used to modify EP-L20. Phenoxy resin is similar to EP, but contains no epoxy groups and is a linear polyether of much higher molecular weight than EP. An acetone solution of Phenoxy (50%) was added to the EP-L20 formulation (20% solid Phenoxy of the blend by weight). The specimen preparation was the same as in the case of PVC. The resulting adhesive joint shear strength of EP-L20 with Phenoxy resin is also higher than EP-L20 and is 132% of the control EP as shown in Fig.8.7.

FIG.8.7 INFLUENCE OF PVC OR PHENOXY COMPONENT ON THE ADHESIVE JOINT SHEAR STRENGTH OF EP-L20 [6]



EP: GY6010-TETA
Lignin: Tomlinite

8.9. WEATHERABILITY

EP-L (AY103/HY956 EP system blended with steam exploded aspenwood lignin) joint specimens with aluminum substrates were exposed to temperature cycling in the environmental chamber (accelerated weathering) for 180 days. There were 720 cycles with the temperature ranging from -30 to 30°C.

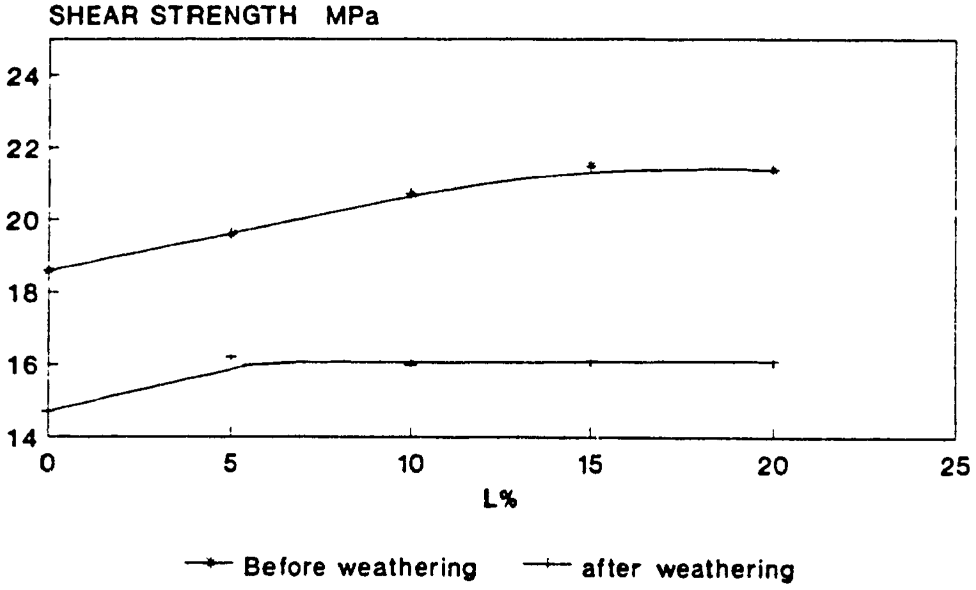
The results of the durability are shown in Fig.8.8. The EP-L polyblends have higher adhesive joint shear strength than EP before accelerated weathering. After 180 days accelerated weathering, the shear strength values of both EP and EP-L polyblends decrease to 77±2% of their controls, and the EP-L polyblends still have higher adhesive joint shear strength than EP. This may be attributed to the presence of lignin which provides the excellent weather durability [222-226].

8.10 PHOTOSTABILITY

EP-L20 joint specimens with aluminum substrates were exposed under a 400 W UV lamp at a distance of 15 cm for 1000 h. The results indicate that the lignin modifier improves the photostability of EP-L20 polyblends as shown in Fig.8.9.

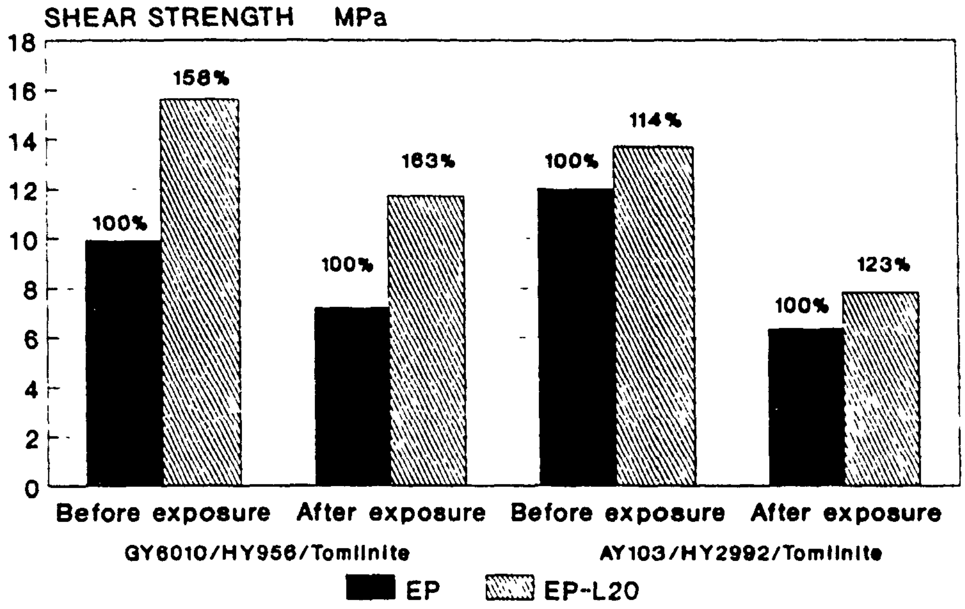
In the case of GY6010/HY956/Tomlinite blend, the adhesive joint shear strength of EP-L20 is 158% of that of the control EP. After 1000 h UV exposure, the strength of EP decreases to 73% of the EP control while the strength of EP-L20 decreases to 75% of the EP-L20 control, and the strength of EP-L20 after exposure is 163% of that of EP.

FIG.8.8 THE ADHESIVE JOINT SHEAR STRENGTH OF EP AND EP-L BLENDS BEFORE AND AFTER ACCELERATED WEATHERING



Weathering condition: •
720 cycles, -30 to 30 C, (180 days)

FIG.8.9 THE ADHESIVE JOINT SHEAR STRENGTH OF EP AND EP-L20 BLENDS BEFORE AND AFTER UV EXPOSURE



1000 h under UV lamp

In the case of AY103/HY2992/Tomlinite blend, the adhesive joint shear strength of EP-L20 is 114% of that of the control EP. After 1000 h UV exposure, the strength of EP decreases to 53% of the EP control while the strength of EP-L20 decreases to 57% of the EP-L20 control, and the strength of EP-L20 after exposure is 123% of that of EP.

8.11 SUMMARY

A wide variety of commercial EP prepolymers, hardeners, lignins, mineral fillers and a third polymeric component are available to be employed in EP-L polyblends with an improvement of the adhesive properties. This is a significant impulse for the utilization of various lignins in epoxy adhesive systems.

The effects of different EP prepolymers, hardeners, lignins and additives on the EP-L adhesive properties are as follows.

Hardwood lignins (Tomlinite, Eucalin, steam exploded lignin) impart a better adhesivity to EP-L than softwood lignin (Indulin). Tomlinite kraft lignin gives the highest adhesive joint shear strength to EP-L20. The improvement can be correlated with the molecular weight of lignin.

A variety of EP-hardener systems can be blended with lignin, resulting in an improved adhesive joint shear strength, which may vary from 112% to 178% of the control EP for different EP-hardener systems.

The adhesive joint shear strength of EP-L is not significantly affected by the addition of 20% mineral fillers.

Besides epoxy and lignin, a third polymeric component such as PVC or Phenoxy resin contributes to the obtaining of better adhesive properties.

The durability tests show that EP-L adhesives have better weatherability and photostability than the control epoxy adhesives. This may be attributed to the presence of lignin which provides better weather durability.

CHAPTER 9

CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE RESEARCH

9.1 CONCLUSIONS

Synthetic polymer (epoxy)-lignin polyblends as structural adhesives with significantly improved adhesive properties, durability and cost advantages have been developed by an effective and economical polyblending technique. As novel polyblends, their surface properties, miscibility and chemical interaction mechanism have been established by extensive modern research techniques.

Based on the results obtained in this study, the following conclusions may be made.

(1) POLYBLENDING

As an alternative to chemical modification of lignin, which is usually carried out in a high temperature chemical process or catalytic reaction, lignin is directly used in an EP-L system, without modification, by a polyblending technique at room temperature, resulting in an improvement of adhesive joint shear strength up to 178% of that of the control EP and a considerable cost advantage. This effective and economical blending technology provides an alternative approach to the current art (chemical synthesis) in developing a polymer-lignin system and is of great significance in cultivating a market for lignin.

(2) FACTORS WHICH EFFECT ADHESIVE JOINT SHEAR STRENGTH

Some important factors which influence the adhesive joint shear strength of EP-L have been established:

(i) The adhesive joint shear strength of EP-L increases as the curing temperature increases. An elevated curing temperature above the Tg of EP leads to a significant improvement in adhesive properties.

(ii) The adhesive joint shear strength of EP-L increases as the amount of lignin increases with an optimal amount of 20% by weight.

(3) INFLUENCE OF VARIOUS COMPONENTS ON ADHESIVE PROPERTIES

A wide variety of commercial EP prepolymers, hardeners, lignins, mineral fillers, third polymeric components and organofunctional silane coupling agents have been employed in EP-L polyblends with a significant improvement in adhesive properties. This is an important impulse for an extensive utilization of lignins in epoxy adhesive systems.

(4) DURABILITY

The EP-L adhesives exhibit superior durability properties:

(i) The accelerated weathering test for 720 cycles from -30°C to 30°C and the UV exposure (1000 h) test show that the weather durability of EP-L is superior to that of the control EP. This may be attributed to the natural polymer (lignin) in the polyblends, which has excellent weather durability.

(ii) The water resistance of EP-L can be significantly improved by introduction of organofunctional silane coupling agents (2% by weight) to EP-L.

(5) SURFACE PROPERTIES

Surface thermodynamic parameters, θ, γ_s, γ^d_s, γ^p_s, W_a, γ_{sl}, S_c and ϕ were determined for EP, EP-L and EP-L10-silane using water and methylene iodine as test liquids. W_a, W_{al}, γ_{12}, and ϕ between these adhesives and the aluminum substrate were also established.

With respect to the wetting and thermodynamic work of adhesion at the adhesive/substrate interface, the following order was found: EP-L-silane> EP-L > EP; the observed adhesive joint shear strength shows the same trend, suggesting a direct correlation between the established surface thermodynamic parameters and the observed adhesive joint shear strength, in both air and water environments.

(6) MISCIBILITY

DSC, DMA, and solid-state CP-MAS NMR spectra were performed on EP-L polyblends with up to 40% lignin to establish the miscibility of the EP-L systems.

The Tg's of the thermal cured EP-L polyblends have a slight trend to increase as the lignin content increases. Only one Tg was detected for the thermal cured blends with up to 20% lignin content, but two Tg's for blends with higher lignin contents. Hence, the EP-L blends with lignin contents up to 20% are miscible. The DMA test indicates that thermal curing causes EP-L polyblends with up to 20% lignin to change from an immiscible system to a miscible system. The agreement is quite good among the results of DSC, DMA and NMR.

These findings not only reveal the basic morphology of these novel materials, but also emphasize their potential application in various material fields since miscible morphology usually gives superior mechanical properties and may give these new EP-L polyblends vast prospects of application as adhesives, coats, sealants, plastics, composites and mortars.

(7) CHEMICAL REACTION MECHANISM

A systematic investigation was conducted for EP-L polyblends to establish the chemical reaction mechanism.

The FTIR spectra clearly indicate the suggested chemical reaction between lignin and the epoxy-polyamine network through their carbonyl and amine groups, respectively, which can occur only under thermal curing conditions in EP-L blends.

Quantitative data concerning the reactivity of lignin towards the polyamine hardener have been determined by a titration method.

Kinetic data indicated that during the EP-L polyblend crosslinking process, the reaction between lignin and polyamine cannot compete with the main reaction between epoxy groups and primary and secondary amines.

Extraction data support the supposition of lignin bonding to the epoxy-polyamine network via unreacted polyamine groups of the hardener.

The lignin bonding to the epoxy-amine network causes the EP-L20 to change from an immiscible blend to a miscible one resulting in the sixfold increase in adhesive joint shear strength.

9.2. RECOMMENDATIONS FOR FUTURE RESEARCH

(1) Polymer-lignin building materials have been reviewed in chapter 2. However, many of these studies are based on chemical synthesis of EP-L. The blending technology may provides an alternative approach not only to EP-L but also to develop various polymer-lignin building materials. This effective and economical technology will provide vast prospects of utilization of lignin in polymer-lignin building materials.

(2) Although several different lignins have been used in this study, there exists many other types of lignin such as

organosolve, wood hydrolysis lignin and so on, which have the potential to be used in EP-L polyblends.

The relation between the physico-chemical properties of various lignins and their performance in EP-L polyblends would be a significant research project.

(3) Future research should include application of EP-L polyblends in coatings, sealants, plastics, composites, mortars and so on.

(4) Following the findings of this study concerning the miscibility and chemical reaction in EP-L, the morphological study using scanning electron microscopy technique is expected to be a very interesting research project.

(5) Further study on the socio-economical aspects of utilization of lignin will be of great significance.

REFERENCES

[1] D. Feldman, D. Banu, C. Luchian, and J. Wang, Journal of Applied Polymer Science, 42, 1307-1318 (1991)

[2] D. Feldman, D. Banu, A. Natansohn, and J. Wang, Journal of Applied Polymer Science, 42, 1537-1550 (1991)

[3] J. Wang and D. Feldman, Journal of Adhesion Science and Technology, Vol.5, No.7, 565-576 (1991)

[4] J. Wang, D. Banu, and D. Feldman, "Epoxy-lignin polyblends", the 33rd IUPAC International symposium on macromolecules, Montreal, Canada, July 1990

[5] J. Wang, and D. Feldman, "Epoxy-lignin polyblends: effect of organosilanes on the adhesive properties", the Materials Research Society, Spring Meeting, Anaheim, CA, USA, April 1991

[6] J. Wang, D. Banu, and D. Feldman, "Epoxy-lignin polyblends: Effect of various components on adhesive properties", accepted by Journal of Adhesive Science and Technology for publication

[7] E.H. Erath and R.A. Spurr, J. Polymer Sci., 35, 390 (1958)

[8] W.G. Potter, Epoxide Resins, Plastics Institute, London, 1970

[9] H. Lee & K. Neville, Handbook of Epoxy Resins, McGraw Hill, New York, 1967.

[10] C.A. May, "Introduction to Epoxy Resins", in C.A. May & Y. Tanaka (Eds), Epoxy Resins: Chemistry and Technology, Marcel Dekker, New York, 1973, pp 1-7.

[11] W.G. Potter, Uses of Epoxy Resins, Chemical Publishing Co., New York, 1976.

[12] F. Lohse, Epoxy Resins: New Results and Developments, Makromol. Chem., Macromol. Symp., 7, 1987, pp 1-16.

[13] P.C. Hewlett & J.D.N. Shaw, "Structural Adhesives Used in Civil Engineering", in: W.C. Wake (Ed), Developments in Adhesives, V.1, Applied Science Publishers Ltd., London, 1977, pp 25-72.

[14] C.J. Fleming & G.E.M. King, " The Development of Structural Adhesives for Three Original Uses in South Africa", International Union of Testing & Research Labs for Materials & Structures, RILEM, Int'l Symp., Paris, Dec. 1967, pp 241-251.

[15] Anon., Araldite Adhesives for the Construction Industry, CIBA-Geigy, Pub. No. M31c, April 1979.

[16] B. Neffgen, Epoxy Resins in the Building Industry - 25 Years of Experience, The Int'l J. of Cement Composites & Lightweight Concrete, V.7, No.4, Nov. 1985, pp 253-260.

[17] G.C. Mays, Structural Applications of Adhesives in Civil Engineering, Materials Science & Technology, V.1, Nov. 1985, pp 937-943.

[18] R. L'Hermite & J. Bresson, "Synthetic Resins in Building Construction", RILEM (reg.18), pp 175-203.

[19] J.R. Panek & J.P. Cook, Construction Sealants and Adhesives, 2nd ed., John Wiley & Sons, New York, 1984, pp 262-317.

[20] P. Maslow, Chemical Materials for Construction, Structures Publishing Co., Farmington, Michigan, 1974, pp 286-319.

[21] Anon., Adhesives: Applications, AJ, V.169, No.18, London, 2 May 1979, pp 923-936.

[22] J. Delmonte, "Adhesives for the Construction Industry", in: C.V. Cagle (Ed), Handbook of Adhesive Bonding, McGraw Hill, New York, 1973, pp 25.1-25.9.

[23] F. Lohse, Epoxy Resins: New Results and Developments, Makromol. Chem., Macromol. Symp., 7 (1987), pp 1-16.

[24] M.J. Bodnar, Durability of adhesive bonded structures, published by John Wiley & Sons (1977).

[25] W.S. Johnson, Adhesively bonded joints, American society for testing and materials (1988)

[26] A.J. Kinloch, J. Mater. Sci., 15 (1980), 2141

[27] A.J. Kinloch, J. Mater. Sci., 17 (1982), 617

[28] R.D. Adams, in: Developments in adhesive-2, A.J. Kinloch (Ed), Applied Science Publishers, London, (1981), p.45.

[29] L.J. Hart-Smith, in: Developments in adhesive-2, A.J. Kinloch (Ed), Applied Science Publishers, London, (1981), p.1.

[30] W.C. Wake, Adhesion and the Formulation of Adhesives, 2nd, Applied Science Publishers, London (1982)

[31] J.M. Harkin, Lignin and its uses., USDA Research Note on FPL 0206 (1969)

[32] Irwin Pearl, Chemistry of Lignin, New York, Marcel Dekker Inc. (1967)

[33] E. Sjostrom, Wood Chemistry, Fundamentals and Applications, New York, Academic Press (1981)

[34] K.V. Sarkanen, et al., Lignin, Occurrence, Formation, Structure and Reaction, New York, Wiley (1971)

[35] Mac Donald et al., Pulp and Paper, New York, McGraw Hill (1969)

[36] N. Shiraishi et al., JP 61 215 610 [86, 215,610] (1986)

[37] D.W. Goheen & C.H. Hoyt, "Lignin", in: Encyclopedia of Chemical Technology, 3rd ed., Kirk, Othmers Eds, V.14, Wiley, Interscience (1978), pp 294-311.

[38] L.H. Sperling & C.E. Carraher, "Renewable Resource Monomers and Polymers", in: Sperling & Carraher (Eds), Polymer Applications of Renewable-Resource Materials, Polym. Sci. & Tech., V.17, Plenum Press, New York (1981) pp 6-7.

[39] S.Y. Lin, " Lignin Utilization: Potential and Challenge", in: D.A. Tillman & E.C. Jahn, (Eds), Progress in Biomass Conversion, V.4, Academic Press, New York (1983), pp 32-78.

[40] K. Kringstad, "The Challenge of Lignin", in: L.E. St. Pierre & G.R. Brown (Eds), Future Sources of Organic Raw Materials, CHEMRAWN I, Pergamon Press, New York, 1980, pp 627-636.

[41] R.G. Nicholas, US Patent, 2 854 422 (1958)

[42] D. Feldman, Phenoplasts from Lignin, Celluloza Hirtie (Bucharest), V12 (8-9), (1963), pp 275-280.

[43] C.W. Montgomery, US Patent, 3 330 788 (1967)

[44] A. Fuhrmann, in" Proceedings of the 5th Int'l Congr. of Scandinavian Chemical Engineers, Bellacent, Copenhagen (1980) pp 526-535.

[45] I. Genov, DMP, V.26, No.5 (1983) pp 1380-1390.

[46] I. Chodak et al., Blends of Polypropylene wit Lignin, Chem. Pap., V.40, No.4 (1986), pp 461-470.

[47] L.M. Beznaczuk, Improving the Durability of Silicone Sealants Through Polyblending, Masters Thesis, CBS, Concordia University, Montreal (1986)

[48] M. Lacasse, Sealant Polyblends with Lignin, Masters Thesis, CBS, Concordia University, Montreal (1986)

[49] D. Feldman et al., "Contribution to the Study of Lignin - Polyurethane & Lignin - Acrylic Polyblends", in: Adhesion 87, 2nd Int'l Cong., Plastics & Rubber Institute, London (1987) pp H1-H6.

[50] J. Guillet, Polymers and Ecological Problems, Plenum Press, New York, 1973, Introduction.

[51] J.R. Kenney, "An Approach to New Polymeric Material via Blocks, Grafts and Blends", in: D. Klempner & K.C. Frisch (Eds), Polymer Alloys, Polym. Sci. & Tech., V.10, Plenum Press, New York, 1977, pp 21-22.

[52] J.A. Manson et al., Polymer Blends and Composites, Plenum Press, New York (1976)

[53] D.J. Williams, Polymer Science and Engineering, Prentice Hall Inc., New Jersey, (1971)

[54] O. Olabisi et al., Polymer-Polymer Miscibility, Academic Press, New York (1979)

[55] R.D. Deanin et al., "Practical Properties of Multi-Phase Polymer Systems", in: L.H. Sperling (Ed), Recent Advances in Polymer Blends, Grafts and Blocks, Polym. Sci. & Tech., V.4, Plenum Press, New York, 1974, pp 63-91.

[56] S.Y. Kienzle, Alloys and Blends, 1987, pp 41-43.

[57] J.J. Elmendrop et al., "Some Microrheological Aspects of Polymer Blending", in: J.C.S. Seferis & P.S. Theocaris (Eds), Interrelations Between Processing Structure and Properties of Polymeric Materials, Elsevier Science Publishers, Amsterdam, 1984, pp 219-227.

[58] M.T. Shaw et al., "Phase Equilibria in Polymer Melts by Melt Titration:, in: C.D. Han (Ed), Polymer Blends and Composites in Multiple Systems, American Chemical Society, Washington D.C. (1984)

[59] L.C.-F. Wu et al., J. Appl. Polym. Sci. 29, 1111-1123 (1984)

[60] W.G. Glasser et al, J. Appl. Polym. Sci. 29, 1815-1830 (1984)

[61] V.P. Saraf et al., J. Appl. Polym. Sci. 29, 1831-1841 (1984)

[62] T.G. Rials et al., Holzforschung 38 (4), 191-199 (1984)

[63] P.C. Muller et al., J. Adhes. 17, 157-174 (1984)

[64] T.G. Rials et al., Holzforschung 38 (5), 263-267 (1984)

[65] P.C. Muller et al., J. Adhes. 17, 185-206 (1984)

[66] K. Kratzl et al. Lignin and Plastics, the Reaction of Lignin with Phenol and Isocyanates, TAPPI 45, No.2, 113-119 (1962)

[67] T.G. Rials et al., Holzforschung 40 (6), 353-360 (1986)

[68] W.G. Glasser et al., J. Wood Chem. Technol. 4(3), 331-345 (1984)

[69] W.G. Glasser et al., Holzforschung 39(6) 345-53 (1985)

[70] W.G. Glasser et al., J. Appl. Polym. Sci. 36(4), 759-72 (1988)

[71] V.P. Saraf et al., J. Appl. Polym. Sci. 30, 2207-2224 (1985)

[72] V.P. Saraf et al., J. Appl. Polym. Sci. 30, 3809-3823 (1985)

[73] J.J. Lindberg et al., in: Lignin Properties and Materials, W.G. Glasser and S. Sarkanen (Eds), ACS Symposium Series 397, ACS, Washington, D.C., 1989, pp 190-204.

[74] H.H. Moorer, W.K. Dougherty, and F.Y. Ball, U.S. Patent 3 519 581 (1970)

[75] S. Brown, U.S. Patent 4 131 573 (1978)

[76] W.G. Glasser, L.C.-F. Wu, and J.-F. Selin, Wood. Agricult. Residues, 1983, 149-165.

[77] W.G. Glasser, Fourth International Symposium on Wood and Pulping Chemistry, Paris 1987, Vol.I, 45.

[78] K. Kringstad, R. Mörck, A. Reimann, and H. Yoshida, Fourth International Symposium on Wood and Pulping Chemistry, Paris, 1987, Vol.I, 67.

[79] V.P. Saraf, W.G. Glasser, and G.L. Wilkes, J. Appl. Polym. Sci. 1985, 30, 2207-2224.

[80] S.L. Ciemniecki and W.G. Glasser, Polymer 1988, 29, 1021- 1029, 1030-1036.

[81] H.H. Nimz, Lignin-based Wood Adhesives, Wood Adhesives (A. Pizzi, Ed.), Marcel Dekker Inc., N.Y. (1983)

[82] E. Archibald, Adhes. Age, pp 27-29 (July 1982)

[83] T. Sellers, Jr., Adhes. Age, pp 19-22 (July 1981)

[84] J.T. White, Adhes, Age, pp 19-22 (July 1981)

[85] E. Roffael et al., Holzforschung 25,4, 112-116 (1971)

[86] E. Roffael et al., Holzforschung 25,5, 149-155 (1971)

[87] E. Roffael et al., Holzforschung 26,6, 197-202 (1972)

[88] E. Roffael et al., Holzforschung 27,6, 214-217 (1973)

[89] A.J. Dolenko et al., Forest Prod. J. 28,8, 41-46 (1978)

[90] M.R. Clarke et al., U.S. Pat. 4,112,675 (Sept. 1978)

[91] A.G. Campbell et al., J. Adhes. 18,4, 301-314 (1985)

[92] J.W. Adams et al., U.S. Pat. 4,303,999 (Dec. 1981)

[93] J.W. Hollis et al., U.S. Pat. 4,306,562 (Dec. 1981)

[94] K.G. Forss et al., Forest Prod. J. 29, No. 7, 39-43 (1979)

[95] K.C. Shen et al., Proceedings of the 13th Internationa Particleboard Symposium, pp 369-379 (1979)

[96] K.C. Shen et al., Adhes. Age 23, 25-29 (1980)

[97] D.P.C. Fung et al., U.S. Pat. 4,256,846 (1981)

[98] A. Go, Lignin Binder System for the Production of Waferboard, 2nd Waferboard Symposium, Ottawa, June 1982

[99] L. Calvé et al., Can. Pat. Appl. 429,292 (1983)

[100] L. Calvé et al., Adhes, Age, 39-43 August (1984)

[101] F.J. Edler, U.S. Pat. 4,194,997 (13 Jan. 1981)

[102] Anon., Regards sur Forintek, pp 5-6, Forintek Can. Corp. (April 1985)

[103] L. Calvé, J. Appl. Polym. Sci. 28, 1969-1980 (1983)

[104] A.L. Lambuth, U.S. Pat. 4,279,788 (July 1981)

[105] M. Gamo, J. Adhes. Soc. Jap. 14, No.2, 56-66 (1978)

[106] M. Gamo, J. Adhes. Soc. Jap. 15, No.10, 435-439 (1979)

[107] M. Gamo, J. Adhes. Soc. Jap. 19, No.6, 221--225 (1983)

[108] M. Gamo et al., J. Adhes. Soc. Jap. 20, No.2, 50-56 (1984)

[109] E.G. James, U.S. Pat. 257925 (Dec. 1981)

[110] Wm. Schoen, U.S. Pat. 264330 (June 1953)

[111] Robert P. Goyle, U.S. Pat. 3931072 (Jan. 1976)

[112] Philip Albrecht et al., U.S. Pat. 2857288 (Oct. 1958)

[113] Forintek Canada Corp., Ottawa, Canada: Development of Lignin Adhesive, 1981-1982

[114] L. Zhao et al., Linchan Huaxue Yu Gongye 1986, 6(2), 18.

[115] Mitsui Toatsn Chemicala Inc., Tokyo Koho 80, 137 (Oct. 1980)

[116] George T. Maloney, Chemicals from Pulp and Wood Waste Production & Application, 250 (1978)

[117] V.F. Felicetta, U.S. Pat. 3886101 (July 1974)

[118] K. Forss et al., Ger Offen. 346009, (March 1971)

[119] R.C. Gupta et al., Chem. Abstr., 90, 6697 (1979)

[120] J.W. Adams et al., Chem. Abstr., 96, 70149 (1982)

[121] W.G. Glasser et al., Chem. Abstr., 96, 54099 (1982)

[122] J.W. Hollis and M.W. Schoenherr, U.S. Pat. 4,303,562 (Dec. 1981)

[123] K.G. Forss and A. Fuhrmann, Forest Prod. J. 29, No.7, 39-43 (1979)

[124] K.C. Shen and L. Calvé, Proceedings of the 13th International Particleboard Symposium, pp 369-379 (1979)

[125] W.G. Glasser et al., Polymer Bulletin 12, 1-5 (1984)

[126] I. Chodak et al., Chem. Papers, 40,(4), 1986, 4610470.

[127] C. Klason et al., Plastics & Rubber Processing & Applications, 6(1), 1986, 17-20.

[128] W.G. Glasser et al., Appl. Polym. Symp., No.28, 297-307 (1975)

[129] W.G. Glasser et al., U.S. Pat. 4,017,474 (1977)

[130] W.G. Glasser et al., Urethane Chemistry & Applications ACS Symp., Symp. Ser. No. 172, 311-338 (1982)

[131] W.G. Glasser et al., ACS Conf. on Food & Agricultural Residues on Uses for Feed, Fuels & Chemicals, Kansas City, 1982, Academic Press, N.Y., 149-166 (1983)

[132] T.G. Rials et al., Holzforschung 38 (5), 269-279 (1984)

[133] H. Yoshida, J. appl. Polym. Sci. 34, 1187-1198 (1987)

[134] Yoshihiro Sono et al., Makuzai Gakkaishi, 33(1) 47-52 (1987)

[135] L.P. Kovrizhnykh et al., Izv. Vyssh. Uchebn. Zaved., Lesn. Zh. 1987, (6), 75-79.

[136] L.P. Kovrizhnykh et al., Khim. Drev. 1988, (1), 90-94.

[137] M. Sadakata, K. Takahashi, M. Saito, and T. Sakai, Fuel, 1967, 66, 1667-1672.

[138] S.R. Beck, M. Wang, Ind. Eng. Chem. Process Des. Dev. 1980, 19, 312.

[139] H. Hatakeyama, Japan Patent 119 091 (1975)

[140] R.B. Phillips et al., J. Appl. Poly. Sci., 1975, 17,443.

[141] J.J. Meister and D.R. Patil, Polym. Mater. Sci. Eng. 52, 235-239 (1985)

[142] J.J. Meister and D.R. Patil, Ind. End. Chem. Prod. Res. Dev. 24, 306-313 (1985)

[143] M. Mihailo et al., Comp Rend. Bulgare Sci. 15, No.2, 155-158, (1962)

[144] F.T. Ball, W.K. Doughty, and H.H. Moorer, Can. Pat. 654, 728 (1962)

[145] N. Shiraishi, in "Lignin Properties and Materials", W.G. Glasser and S. Sarkanen (Eds.), ACS Symposium Series 397, American Chemical Society, Washington, D.C., 1989, pp.488-495.

[146] W.L.S. Nieh and W.G. Glasser, in "Lignin Properties and Materials", W.G. Glasser and S. Sarkanen (Eds.), ACS Symposium Series 397, ACS, Washington, D.C., 1989, pp.506-513.

[147] B. Tomita, A. Kurozumi, and S. Hosoya, in "Lignin Properties and Materials", W.G. Glasser and S. Sarkanen (Eds.), ACS Symposium Series 397, ACS, Washington, D.C., 1989, pp.496-505.

[148] A.H. Landrock, Adhesives Technology Handbook, Noyes Publications, NJ, 1985, pp 187-289.

[149] C.V. Cagle, "Bonding Various Substrates" in: Cagle (Ed.), Handbook of Adhesive Bonding, pp 11, 14-11, 21.

[150] R.A. Fava, Polymer, 9 (1968) 137.

[151] O.R. Abolafia, Soc. Plast. Eng. Tech. Papers, 15 (1969), 610.

[152] W. Manz and J.P. Creedon, Thermal Analysis Proceedings Third ICTA Davos 1971, Birkäuser Verlag, Basel, 1971, Vol.3, p.145.

[153] N.N. Thermal Analysis Application Brief Number 90033, August 1970, Dupont Instruments.

[154] G.A. Zabrzenski, Polymer 14, 347 (1973).

[155] R.L. Chen et al., J. Applied Polym. Sci., V.32, 4815-4826, (1986).

[156] R.L.Blaine and L.Woo, Am. Chem. Soc., Polymer Preprints, 17(2) (1976)

[157] D. Kealble, SPEJ. 15, 1071 (1959)

[158] J.W. Robinson, "Undergraduate Instrumental Analysis", Marcel Dekker Inc., New York, 1987.

[159] J.J. Lindberg et al., Adv. Polym. Sci., 66, 1 (1985).

[160] E.O. Stejkal et al., Macromolecules, 14, 275 (1981).

[161] W. Kolodziejski, J.S. Frye, and G.E. Macier, Anal. Chem., 54, 1419 (1982).

[162] J. Lee and K. Neville, Handbook of Epoxy Resins, McGraw Hill, New York (1967).

[163] D.O. Hummel (Ed.), Polymer Spectroscopy, Verlag Chemie, (1974) p 132.

[164] R.O. Allen and P. Sanderson: Appl. Spectroscopy Rev., Vol. 24, pp 175-187 (1988).

[165] G.C. Stevens: J. Appl. Polym. Sci., Vol. 26, pp 4279-97 (1981).

[166] K.V. Sarkanen et al., "Lignin", a division of John Wiley & Sons, Inc., NY (1971).

[167] B.L. Browning, Methods of Wood Chemistry, Interscience publishers, NY (1967)

[168] L. Birladeanu, IR, Wiley-interscience, NY (1972).

[169] J.L. Hergert, Infrared Spectra in K.V. Sarkanen and C.H. Ludwig (Eds.) Lignins, Occurrence, Formation, Structure and Reactions, Wiley Interscience (1971), p. 267-288.

[170] O. Faix, O. Beinhoff: J. of Wood Chem. and Techn. Vol. 8, pp 505-522 (1988).

[171] J. McMurry, Organic Chemistry, pp 674-675, 910-911, Sec. Ed., Brooks/Cole, New York (1988).

[172] H. Jahn, P. Goetzky, "Analyses of Epoxides and Epoxy Resins", in Epoxy resins, C.A. May and Y. Tanaka (Eds.) pp 685, Marcel Dekker Inc., NY, 1973

[173] J. Pellinen, and M. Salkinoja-Salonen: J. Chromotogr., Vol. 28, pp 297-308, (1985).

[174] O. Goldschmid, Ultraviolet Spectra in K.V. Sarkanen and C.H. Ludwig, (Eds.) "Lignins, Occurrence, Formation, Structure and Reactions", Wiley Interscience (1971) p

241-266.

[175] A. Scalbert, and B. Monties, Holzforsch, Vol.40, pp 119-27 (1986).

[176] K. Lundquist, and T.K. Kirk, Tappi, Vol.63, pp 80-82 (1980)

[177] A.N. Gent, Int. J. Adh. and Adhes. April, 1981, 175.

[178] A. Ahagon, A.N. Gent, J. Polym. Sci. Polym. Phys. Ed. 13, 1285 (1975).

[179] A. Ahagon, A.N. Gent, E.C. Hsu, Adhesion Science and Technology, In: Polymer Science and Technology. Vol.9a, L.H. Lee (ed.) Plenum Press, New York, 1975, 281.

[180] E.P. Plueddemann, Composite Materials, In: Interfaces in Polymer Matrix Composites. Vol. 6, Academic Press, 1974.

[181] E.P. Plueddemann, In: Treatise on coatings. Vol.1, Part III, R.R. Meyers and J.S. Long, Vol.6 Academic Press, 1974.

[182] W.A. Dukes, A.J. Kinloch, Preparation of Surfaces for Adhesive Bonding, Explosive Research and Development Establishment, Watham Abbey, England, 1976.

[183] L. Graham, J.A. Emerson, Adhesion Aspects of Polymeric Coatings, K.L. Mittal. (Ed.) Plenum Press, New York, 1982, p 395.

[184] J.B. Bolger, R.W. Hausslein, H.E. Movlar, Int. Copper Research Assoc., Proj. No. 172, Final Repot, p.2, Amicon Corp., Lexington, MA, 1971.

[185] P. Walker, J. Coat. Tech. 52, No.670, 49 (1980).

[186] H.A. Clark, E.P. Plueddemann, Mod. Plas. 40 (6), 133 (1963).

[187] R.L. Kaas, J.L. Kardos, SPE. 32nd ANTEC, 1976, 22.

[188] W.D. Bascom, Macro molecular 5, 792 (1972).

[189] A.J. Kinloch, Adhesion and Adhesives, Chapman and Hall, London, 1987.

[190] Union Carbide, Organofunctional Silanes, Danbury, 1983.

[191] R.A. Gledhill, A.J. Kinloch, J. Adhesion, 6, 315 (1974).

[192] C. Kerr, N.C. MacDonald, J. Orman, J. Appl. Chem., 17, 62, (1967).

[193] T. Young, Philos. Trans, R. Soc. London 95, 65 (1805).

[194] H.W. Fox and W.A. Zisman, J. Colloid Sci. 7, 428 (1952).

[195] G.M. Fowkes, J. Phys. Chem. 67, 2538 (1963).

[196] D.K. Owens and R.C. Wendt, J. Appl. Polym. Sci. 13, 1741 (1969).

[197] D.H. Kaelble, J. Adhesion 2, 66 (1970).

[198] S. Wu, J. Polym. Sci. Part C 34, 19 (1971).

[199] S. Wu, Polymer Interface and Adhesion, Marcel Dekker, New York (1982).

[200] Y.C. Ko, B.D. Ratner and A.S. Hoffman, J. Colloid Interface Sci. 82, 25 (1981).

[201] J.W. Lin, P. Dudek and D. Majumdar, J. Appl. Polym. Sci. 33, 657 (1987).

[202] A. El-Shimi and E.D. Goddard, J. Colloid Interface Sci. 48, 243 (1974).

[203] R.A. Pyter, G. Zografi and P. Mukerjee, J. Colloid Interface Sci. 89, 144 (1982).

[204] R.N. King, J.D. Andrade, S.M. Ma, De.E. Gregonis and L.R. Brostner, J. Colloid Interface Sci. 103, 62 (1985).

[205] K.T. Varughese, P.P. De and S.K. Sanyal, J. Adhesion Sci. Technol. 3, 541-550 (1989).

[206] R.G. Schmidt and J.P. Bell, J. Adhesion Sci. Technol. 3, 515-527 (1989).

[207] A. Drupré, Théore Mechanique de la Chaleur, p.369. Gauthier-Villars, Paris (1969).

[208] B.W. Cherry, Polymer Surfaces. Cambridge University Press, London (1981).

[209] L.A. Girifalco and R.J. Good, J. Phys. Chem. 61, 904 (1957).

[210] K.L. Mittal, Polym. Eng. Sci. 17, 467 (1977)

[211] S. Wu, J. Adhesion 5, 44 (1973).

[212] D.H. Kaelble, J. Adhesion 1, 102 (1969).

[213] M. Levine, G. Ilkka and P. Weiss, J. Polym. Sci. B2, 915 (1964).

[214] R. Kruger and H. Potente, J. Adhesion 11, 113 (1980).

[215] B.W. Cherry and S. El Muddarris, J. Adhesion 2, 42 (1970).

[216] T. Smith and D.H. Kaelble, in: Treatise on Adhesion and Adhesives, R. Patrick (Ed.), Vol. R, pp.139-292, Marcel Dekker, New York (1981).

[217] K.L. Mittal, in: Adhesion Science and Technology, Part A, L.H. Lee (Ed.), p.153, Plenum Press, New York(1975)

[218] T. Sellers Jr. et al., Forest Products Research Society Madison, Wi. Proceedings No. 47359 (1988).

[219] R.1 Morck et al., Holzforschung,40, Suppl. 51-60 (1986)

[220] H. Yoshida et al., J. Applied Polymer Sci.,34, 1187-1198 (1987).

[221] R. Morck et al., Holzforschung,42, 111-116 (1988)

[222] V.E. Gul et al., Polym. Mech. 1965, 1.

[223] K. Levon et al., J. Polymer 1987, 28, 745-750.

[224] V.E. Bronovitskii, A. Plast, Massy 1977, 1, 34.

[225] P. Tormala et al., Paper & Timber 1972, 54, 158.

[226] N.S. Allen, In New Trends in the Photochemistry of Polymers, Elsevier Appl. Sci. Publ., London, 1985, 209-246.

APPENDIX 1

STANDARD DEVIATION DATA OF ADHESIVE JOINT SHEAR STRENGTH (MPa) IN FIGURES

MEAN VALUE	$X = 1/n \Sigma X_i$	$n=5-10$
VARIANCE	$Var(X) = 1/n \Sigma (X_i - X)^2$	
STANDARD DEVIATION	$\sigma_x = Var(X)^{0.5}$	
COEFFICIENT OF VARIATION	$COV = \sigma_x/X$	

[1] FIG.3.1

TEMP. °C	X	Var(X)	σ_x	COV
23	1.15	0.04	0.18	0.16
75	7.85	1.48	1.22	0.16
100	10.2	5.53	2.35	0.23
120	10.5	1.39	1.18	0.11

[2] FIG.3.2

EP-L20:

DAYS	X	Var(X)	σ_x	COV
0	21.5	0.38	0.61	0.03
1	14.6	0.66	0.81	0.06
3	11.9	2.85	1.69	0.14
7	11.3	1.13	1.06	0.09

EP:

DAYS	X	Var(X)	σ_x	COV
0	12.1	0.55	0.74	0.06
1	7.88	1.20	1.09	0.14
3	6.38	0.43	0.66	0.10
7	6.38	0.72	0.85	0.13

[3] FIG.3.3

BLENDS	X	Var(X)	σ_x	COV
EP	12.1	0.26	0.51	0.04
EP-L10	18.5	2.43	1.56	0.08
EP-L20	21.5	0.38	0.61	0.03
EP-L25	16.9	0.30	0.55	0.03
EP-L30	14.9	1.99	1.41	0.10
EP-L40	10.2	5.53	2.35	0.23

[4] FIG.6.1

%	X	Var(X)	σ_x	COV
0	9.4	0.77	0.88	0.09
0.5	13.1	1.32	1.15	0.09
1.0	14.6	0.95	0.97	0.07
2.0	14.6	2.26	1.50	0.10
5.0	12.8	1.61	1.27	0.10

FIG.6.2

EP-Silane:

BLENDS	X	Var(X)	σ_x	COV
EP	8.4	1.05	1.03	0.12
EP-A189	13.5	0.44	0.66	0.05
EP-A1110	12.3	1.99	1.41	0.11
EP-A187	13.5	0.32	0.56	0.04

EP-L10-Silane:

BLENDS	X	Var(X)	σ_x	COV
EP-L10	9.4	0.77	0.88	0.09
EP-L10-A189	14.3	2.02	1.42	0.10
EP-L10-A1110	14.6	2.26	1.50	0.10
EP-L10-A187	14.9	5.63	2.37	0.16

FIG.6.3

DLENDS	X	Var(X)	σ_x	COV
EP	0.1	0.0004	0.02	0.20
EP-L10	2.0	0.1	0.32	0.16
EP-L10-A187	9.3	1.55	1.24	0.13

FIG.6.4

CONTROL:

DLENDS	X	Var(X)	σ_x	COV
EP	8.4	1.05	1.03	0.12
EP-L10	9.4	0.77	0.88	0.09
EP-L10-A187	14.9	5.63	2.37	0.16

WATER:

DLENDS	X	Var(X)	σ_x	COV
EP	0.1	0.01	0.01	0.00
EP-L10	2.0	0.1	0.32	0.16
EP-L10-A187	9.3	1.55	1.24	0.13

FIG.6.5

BLENDS	X	Var(X)	σ_x	COV
EP	6.57	0.46	0.68	0.10
EP-L10	9.39	0.82	0.90	0.10
EP-L10-A189	11.4	1.62	1.27	0.11
EP-L10-A187	12.8	0.58	0.76	0.06
EP-L10-A1110	14.3	3.47	1.86	0.13

FIG.6.6

CONTROL:

BLENDS	X	Var(X)	σ_x	COV
EP	8.4	1.05	1.03	0.12
EP-L10	9.4	0.77	0.88	0.09
EP-L10-A189	14.3	2.02	1.42	0.10
EP-L10-A187	14.9	5.65	2.37	0.16
EP-L10-A1110	14.6	2.26	1.50	0.10

UV:

BLENDS	X	Var(X)	σ_x	COV
EP	6.57	0.46	0.68	0.10
EP-L10	9.39	0.82	0.90	0.10
EP-L10-A189	11.4	1.62	1.27	0.11
EP-L10-A187	12.8	0.58	0.76	0.06
EP-L10-A1110	14.3	3.47	1.86	0.13

FIG.8.2

EP-L20:

BLENDS	X	Var(X)	σ_x	COV
EP	9.9	0.99	0.99	0.10
EP-TO	15.6	0.28	0.53	0.03
EP-IN	12.2	0.70	0.84	0.07
EP-AT	12.7	4.17	2.04	0.16
EP-SE	13.8	1.99	1.41	0.10

EP-L40:

BLENDS	X	Var(X)	σ_x	COV
EP	9.9	0.99	0.99	0.10
EP-TO	10.5	1.51	1.23	0.12
EP-IN	10.2	1.06	1.03	0.10
EP-AT	12.3	0.12	0.35	0.03
EP-SE	13.1	1.03	1.02	0.08

FIG.8.3

BLENDS	X	Var(X)	σ_x	COV
EP-L10(I)	3.3	0.21	0.46	0.14
EP-L10(II)	10.0	0.59	0.77	0.08
EP-L10(III)	11.6	0.27	0.52	0.05
EP-L10(UF)	9.4	0.13	0.36	0.04

FIG.8.4

CA1200-HY2991:

DLENDS	X	Var(X)	σ_x	COV
EP	12.1	0.26	0.51	0.04
EP-L20	21.5	0.38	0.61	0.03
EP-L40	10.2	5.53	2.35	0.23

CY6010-HY956:

DLENDS	X	Var(X)	σ_x	COV
EP	9.9	0.99	0.99	0.10
EP-L20	15.6	0.28	0.53	0.03
EP-L40	10.5	1.51	1.23	0.12

AY103-HY2992:

DLENDS	X	Var(X)	σ_x	COV
EP	12.0	0.57	0.76	0.06
EP-L20	13.7	0.53	0.73	0.05
EP-L40	10.3	0.04	0.21	0.02

FIG.8.5

GY6010-HY956:

DLENDS	X	Var(X)	σ_x	COV
EP	9.9	0.99	0.99	0.10
EP-L20	15.6	0.28	0.53	0.03
EP-L40	10.5	1.51	1.23	0.12

CY6010-HY2992:

DLENDS	X	Var(X)	σ_x	COV
EP	9.7	0.71	0.84	0.09
EP-L20	12.9	1.67	1.29	0.10
EP-L40	11.1	0.99	1.00	0.09

GY6010-TETA:

DLENDS	X	Var(X)	σ_x	COV
EP	8.4	1.05	1.03	0.12
EP-L20	9.4	0.37	0.61	0.07
EP-L40	10.2	0.16	0.40	0.04

FIG.8.6

GY6010-HY956:

DLENDS	X	Var(X)	σ_x	COV
EP	9.9	0.99	0.99	0.10
EP-L20	15.6	0.28	0.53	0.03
EP-L20-AG20	15.6	3.06	1.75	0.11

GY6010-HY2992:

BLENDS	X	Var(X)	σ_x	COV
EP	9.7	0.71	0.84	0.09
EP-L20	12.9	1.67	1.29	0.10
EP-L20-AG20	12.6	2.34	1.53	0.12
EP-L20-Si20	13.3	1.02	1.01	0.08
EP-L20-Al20	12.3	2.56	1.60	0.13

FIG.8.7

BLENDS	X	Var(X)	σ_x	COV
EP	8.4	1.05	1.03	0.12
EP-L20	9.4	0.37	0.61	0.06
EP-L20-PHENOXY20	11.1	0.63	0.79	0.07
EP-L20-PVC20	15.9	5.33	2.31	0.15

FIG.8.8

BEFORE WEATHERING

LIGNIN %	X	Var(X)	σ_x	COV
0	18.6	0.58	0.76	0.04
5	19.6	3.33	1.83	0.09
10	20.7	0.84	0.91	0.04
15	21.5	0.59	0.77	0.04
20	21.4	0.39	0.62	0.03

AFTER WEATHERING

LIGNIN %	X	Var(X)	σ_x	COV
0	14.7	0.76	0.87	0.06
5	16.2	1.41	1.19	0.07
10	16.0	1.36	1.17	0.07
15	16.1	2.11	1.45	0.09
20	16.1	1.43	1.20	0.07

FIG.8.9

GY6010/HY956/TOLINITE:
BEFORE EXPOSURE

DLENDS	X	Var(X)	σ_x	COV
EP	9.9	0.99	0.99	0.10
EP-L20	15.6	0.28	0.53	0.03

AFTER EXPOSURE

DLENDS	X	Var(X)	σ_x	COV
EP	7.2	0.50	0.71	0.10
EP-L20	11.7	0.47	0.69	0.06

AY103/HY2992/TOMLINITE:
BEFORE EXPOSURE

DLENDS	X	Var(X)	σ_x	COV
EP	12.0	0.57	0.76	0.06
EP-L20	13.7	0.53	0.73	0.05

AFTER EXPOSURE

DLENDS	X	Var(X)	σ_x	COV
EP	6.3	0.93	0.97	0.15
EP-L20	7.8	1.31	1.15	0.15

APPENDIX 2

STANDARD DEVIATION DATA OF CONTACT ANGLE (DEGREE) IN TABLE.7.1

MEAN VALUE	$X = 1/n \Sigma X_i$	$n=10$
VARIANCE	$Var(X) = 1/n \Sigma (X_i - X)^2$	
STANDARD DEVIATION	$\sigma_x = Var(X)^{0.5}$	
COEFFICIENT OF VARIATION	$COV = \sigma_x/X$	

TABLE.7.1

WATER.

SURFACE	X	Var(X)	σ_x	COV
EP	81	5.0	2.2	0.03
EP-L10	75	5.0	2.2	0.03
EP-L10-A187	69	2.2	1.5	0.02

METHEYLENE IODIDE:

SURFACE	X	Var(X)	σ_x	COV
EP	50	3.6	1.9	0.04
EP-L10	38	1.7	1.3	0.04
EP-L10-A187	18	1.9	1.4	0.08