# DEVELOPMENT OF A WATERBASED POLYCHLOROPRENE ADHESIVE

BY

# LALITH GREGORY WICHRAMASSIGHE

MSc (Polymer Science & Technology) - 1999

The work described in this thesis was carried out by me under the supervision of Mr J.T.S Motha and Dr Sudanth Liyanage and a report on this has not been submitted to any other University for another degree.

daux in bay

L.G. Wickramasinghe

We certify that the above statement made by the candidate is true and that this thesis is suitable for submission to the University for the purpose of evaluation.

Dr Sudantha Liyanage

5.170 

J.T.S Motha

## DEVELOPMENT OF A WATERBASED POLYCHLOROPRENE ADHESIVE

BY

#### LALITH GREGORY WICKRAMASINGHE

Thesis submitted to the University of Sri Jayewardenepura for the partial fulfilment of the requirement for the award of the degree of Master of Science in Polymer Science & Technology.

## TABLE OF CONTENTS

Table of contents	Page I
Abbreviations	V1I
List of figures	VII1
List of Tables	1X
Acknowledgement	X1
Abstract	XII
1.0 CHAPTER ONE - INTRODUCTION	1
1.1 Types of adhesives	3
1.1.1 Solvent based adhesives	3
1.1.2 Water based adhesives	3
1.1.3 Solventless adhesives	3
1.2 Classification of adhesives	5
1.3 Rubber based adhesives	8
1.4 Polychloroprene in contact adhesives	9
1.4.1 Acetylene process	10
1.4.2 Butadiene process	10
1.5 Polymerisation of chloroprene and structure of polychloroprene	12
1.5.1 Emulsion polymerisation	12
1.5.2 Neoprene process	13
1.5.3 Polymer microstructure	14
1.6 Structure of polychloroprene rubber and effects on adhesive properties	17

1.7	Vucanisate properties of polychloroprene	19		
1.	8 The application on polychloroprene rubber	20		
1.	9 Criteria for differentiation of polychloroprene grades	20		
1.	10 Typical formulation of a solvent based polychloroprene	21		
	adhesive			
1.	1 Forces driving changes in solvent based formulations	22		
1.	12 Limitations on the usage of organic solvents in adhesives	23		
1	13 Alternatives to solvent based adhesives	23		
1	14 Need for development of a water based polychloroprene adhesive	24		
1	.15. Water based polychloroprene adhesive	24		
1	.16 Mechanism of solvent based polychloroprene adhesive	25		
1	.17 Mechanism of a water based polychloroprene adhesive	27		
2.0 CHAPTER TWO - MATERIAL AND EXPERIMENTIAL METHOD				
2.1 Material - Compounding Ingredients				
	2.1.1 Polychloroprene latex	30		
	2.1.2 Phenolic resin	31		
	2.1.3 Acid acceptor	33		
	2.1.4 Antioxidant	33		
	2.1.5 Vinyl acrylic	34		
	2.1.6 Curing/ Vulcanising agents	34		
	2.1.7 Thickeners	35		
	2.1.8 Fillers	36		
	2.1.9 Dispersing agent and wetting agent	36		

# II

	2.1.10 Biocide	36
2.2	Experimental Method	37
	2.2.1 Preparation of zinc oxide -50% solid aqueous dispersion	37
	2.2.2. Preparation of antioxidant -33% solid aqueous dispersion	38
	2.2.3 Carboxylated polychloroprene latex adhesive formulation	40
	2.2.4 Carboxylated polychloroprene adhesive formulation with varying phenolic resin content.	41
	2.2.5 Non carboxylated polychloroprene latex adhesive formulation	42
	2.2.6 Non carboxylated polychloroprene adhesive formulation with varying phenolic resin content.	43
	2.2.7 The synergistic effects on carboxylated polychloroprene latex and acrylics in water based adhesives.	44
	2.2.8 Preparation of sulphur 50% aqueous dispersion.	46
	2.2.9 Preparation of ZDEC 33% aqueous dispersion.	46
	2.2.10 Introduction of sulphur and accelerator system to the formulation	47
2.3	Equipment and Machinery	48
	2.3.1 Ball mill	48
	2.3.2 Stirrers / blending vessel	49
2.4 P	reservation of water based adhesives	50
2.5 Th of	he effects of fumed metallic oxides on the rheological properties water based adhesives	51
2.6 T	he effect of temperature on polymeric adhesives	51

<ul> <li>3.0 CHAPTER THREE - TEST PROCEDURE</li> <li>3.1 Testing on adhesives.</li> <li>3.1.1 Testing of working properties</li> </ul>			53
			54
			54
3.1.1.1	L.Storage li	fe	54
3.1.1.2	2 Pot life / v	working life	55
3,1,1,3	3 Coverage		56
3.1.1.4	4 Blocking		56
3.1.1.5	5 Consister	су	56
3.1.1.0	5 Tack		57
3.1.1.7	7 Penetratio	on	57
3.1.1.8	3 Curing ra	te	58
3.1.2 Physica	l testing of	adhesives bonds	58
3.1.2.1	Test for s	trength parameters	59
	3.1.2.1.1	Bond strength	59
	3.1.2.1.2	Shear strength	59
	3.1.2.1.3	Peel strength	59
	3.1.2.1.4	Flexural strength	60
	3.1.2.1.5	Impact strength	61
	3.1.2.1.6	Cleavage strength	61
	3.1.2.1.7	Fatigue strength	62
3.1.2.2	2 Adhesive condition	testing against environmental	62
	3.1.2.2.1	Durability - testing	62
	3.1.2.2.2	Chemical factors	63

	3.1.2.2.3 Biological	63
	3.1.2.2.4 Temperature	64
	3.1.2.2.5 Ageing or weathering	64
	3.1.2.2.6 Radiation	65
3.2	Test methods on water based adhesives	65
	3.2.1 Total solid content	65
	3.2.2 Viscosity	66
	3.2.3 Determination of shear strength	68
	3.2.4 Determination of peel strength	72
4.0 CHAP	TER FOUR - TEST RESULTS & DISCUSSION, CONCLUSION & SUGGESTIONS	75
4.1	Test results and discussion.	76
	4.1.1 Test results of bond strength in relation to varied phenolic resin content (carboxylated polychloroprene latex)	77
	4.1.2 Bond strength vs phenolic resin content	79
	4.1.3 Test results of bond strength in relation to varied phenolic resin content (non carboxylated polychloroprene latex)	81
	4.1.4 Bond strength vs phenolic resin content	81
	4.1.5 Synergistic effect on carboxylated polychloroprene latex and acrylics in water based adhesives	83
	4.1.6 Test results of bond strength of caboxylated polychloroprene latex blended with varied vinyl acrylic co-polymer content.	84
	4.1.7 Test results of bond strength of caboxylated polychloroprene latex blended with varied pure acrylic	85

	4.1.8 Carboxylated polychloroprene latex blended with vinyl acrylic / pure acrylic in combination with sulphur and accelerator vulcanising system	87
	4.1.9 Test results of carboxylated polychloroprene latex blended with vinyl acrylic / pure acrylic in combination with sulphur and accelerator vulcanising system	88
	4.1.10 The types of adhesives formulated for the bonding of unvulcanised rubber foxing to canvas upper	89
	41.11 Comparison of bond strength results of solvent based polychloroprene adhesive against water based carboxylated polychloroprene adhesive	90
	4.1.12 Wet/dry bond strength comparison of water based polychloroprene adhesive	91
	4.1.13 Final formulation	92
	4.1.14 The product specification of the water based polychloroprene adhesive	92
	4.1.15 Flow diagram of mixing	93
	4.1.16 The test results of the final adhesive	94
	4.1.17 Cost Analysis	95
	4.1.17.1 Costing of polychloroprene solvent based adhesives as per typical formulation	96
	4.1.17.2 Costing of water based polychloroprene adhesives	97
	4.1.17.3 Costing of zinc oxide dispersion- 50% solids	98
	4.1.17.4 Costing of antioxidant dispersion- 33% solid	99
	4.1.17.5 Cost of the final product	100
4.2	Conclusion and suggestion for further development	102
	4.2.1 Conclusion	102
	4.2.2 Suggestions for further development	103
References	3	104

VI

## **ABBREVIATIONS**

•	ASTM	- American society of testing and material
•	BS	- British Standards
•	CIF	- Cost, insurance and freight
•	GST	- Goods and services tax
•	MEK	- Methyl ethyl ketone
•	phr	- Parts per hundred rubber
•	TEC	- Trichloroethane

- Tg Glass transition temperature
- Tm Crystalline melting temperature
- VOC Volatile organic compound
- ZDEC Zinc diethyl dithiocarbamate

## LIST OF FIGURES

Deee

		rage
1.1	Classification of adhesives	7
1.2	Types of adhesive based on different rubbers	9
1.3	Neoprene process	13
1.4	Configurations on monomer units in polymer chain	14
1.5	Effect of crystallinity on polymer properties	16
1.6	Effects of solution, gel and curing and polymer properties	16
1.7	Structure of polychloroprene	17
1.8	Solvent based polychloroprene adhesive formulation	21
1.9	Mechanism of solvent based polychloroprene adhesive	26
1.10	Mechanism of water based polychloroprene adhesive	28
2.1	Ball Mill	48
2.2	Stirrers & blending vessel	49
2.3	Flow pattern in a blending vessel	49
3.1	Brookfield Viscometer	67
3.2	Test specimen of determination of shear strength	70
3.3	Metal roller	70
3.4	Test specimen of determination of peel strength	73
4.1	Bond strength vs phenolic resin content	79
4.2	Bond strength vs phenolic resin content	81
4.3	Flow diagram of mixing	93

# LIST OF TABLES

1.1	Effects on polymerisation parameters	15
1.2	Elastomeric adhesives	19
2.1	Formulation of zinc oxide 50% dispersion	37
2.2	Formulation of antioxidant 33% dispersion	38
2.3	Formulation of carboxylated polychloroprene latex adhesive (F-1)	40
2.4	Formulation of polychloroprene adhesive by varing phenolic resin content (F-1)	41
2.5	Formulation of non carboxylated polychloroprene latex adhesive (F-2)	42
2.6	Formulation of non carboxylated polychloroprene adhesive by varing phenolic resin content (F-2)	43
2.7	Formulation of carboxylated polychloroprene latex blended with acrylics in adhesive formulation (F-3)	44
2.8	Formulation of sulphur 50% aqueous dispersion	46
2.9	Formulation of ZDEC 33% aqueous dispersion	46
2.10	Formulation with sulphur / accelerator system (4-4)	47
3.1	Bs and ASTM procedures for total solid content	66
4.1	Formulation of carboxylated polychloroprene adhesive by varing the phenolic resin content (F-1)	77
4.2	Test results of bond strength in relation to varied phenolic resin content (carboxylated polychloroprene latex)	77
4.3	Formulation of non carboxylated polychloroprene adhesive by varing phenolic resin content (F-2)	80
4.4	Test results of bond strength in relation to varied phenolic resin content(non carboxylated polychloroprene latex)	81

4.5	Formulation of water based adhesive with carboxylated polychloroprene latex and acrylics (F-3)	83
4.6	Test results of bond strength of carboxylated polychloroprene latex blended with varied vinyl acrylic co-polymer content	84
4.7	Test results of bond strength of carboxylated polychloroprene latex blended with varied pure acrylic co-polymer content	85
4.8	Carboxylated polychloroprene latex blended with vinyl acrylic / pure acrylic in combination with sulphur and accelerator vulcanising system.	87
4.9	Test results of carboxylated polychloroprene latex blended with vinyl acrylic / pure acrylic in combination with sulphur and accelerator vulcanising system.	88
4.10	The types of adhesive formulated for the bonding of unvulcanized rubber foxing to canvas upper.	89
4.11	Comparison of bond strength results of solvent based polychloroprene adhesive against water based carboxylated polychloroprene adhesive.	91
4.12	Wet/Dry bond strength comparison of water based polychloroprene adhesive	91
4.13	Final formulation	92
4.14	The test results of the final adhesive	94
4.15	Costing of polychloroprene solvent based adhesive	96
4.16	Costing of water based polychloroprene adhesive	97
4.17	Costing of zinc oxide dispersion 50% solids	98
4.18	Costing of antioxidant dispersion 33% solids	99
4.19	Cost of final product	100

#### ACKNOWLEDGEMENTS

I wish to express my sincere thanks to my supervisors Mr. J.T.S. Motha, Manager Rubber and Plastic Division of Industrial Technology Institute and to Dr Sudanth Liyanage of the University of Sri Jayewardenepura for their inspiring guidance and encouragement throughout the research project and in the preparation of this thesis.

I wish to express my gratitude to the Director of the Industrial Technology Institute for the facilities extended to pursue my research work at the institute and to the staff of the Rubber & Plastic Division for their support and assistance provided during my research project.

I also take this opportunity to thank M/s Du-Pont Singapore Pte Ltd of Singapore and M/s Schenectady International of U.S.A and M/s Myung Kwang Chemical Co Ltd of Korea and the other chemical suppliers and their local agents who arranged samples for this research project.

Special expression of thanks to my friends and colleagues who helped me in many ways for the successful completion of my research project and preparation of the thesis and finally, I thank my parents and to my eldest brother for their continued support and encouragement throughout my formal education.

XI

#### DEVELOPMENT OF A WATERBASED POLYCHLOROPRENE ADHESIVE

By

Lalith Gregory Wickramasinghe

#### ABSTRACT

Adhesive is a substance capable of holding material together by surface attachment. The adhesives are either natural or synthetic, organic or inorganic compounds which are commonly polymeric material. Adhesion is interaction that develops between two substrates when they are in contact with an adhesive and is thus a multidisciplinary science dealing with the chemistry and physics of surface and interfaces as well as the mechanics of deformation and fracture of an adhesive bond. Polychloroprene rubber is one of the most widely used and certainly one of the most versatile polymers, ever developed for use as an adhesive base material. Polychloroprene is produced by the emulsion polymerisation process and it is commercially available in solid form as well as in an aqueous dispersion in latex form. The most common and the established polychloroprene adhesive is the solvent based polychloroprene contact adhesive which has been in the market for many years.

The environmental concerns (ozone depletion and smog), health hazard to industrial workers, governments imposing heavy taxes and restrictions on the use of solvents with high VOC, phasing out production of solvents with high VOC and the antisocial impact as a result of sniffing of solvent based adhesives, have created a world wide concern for the use of solvent based adhesives. In considering the above factors the alternatives to solvent based adhesives are hundred percent solid adhesives e.g. hot melt adhesives or water based adhesives.

In this study the theme is to produce an environmental friendly, cost effective water based polychloroprene adhesive to over come the above mentioned factors on solvent based adhesive systems.

Trials were carried out with non carboxylated and carboxylated polychloroprene latex. A water based polychloroprene latex adhesive was formulated by blending the carboxylated polychloroprene latex with dispersions of alkyl phenolic resin, zinc oxide, antioxidant and an aqueous solution of a biocide in the presence of a dispersing agent in the blend. Further improvements were made to the formulation by introducing a vinyl acrylic with the carboxylated polychloroprene latex as the base material in order to enhance the adhesive properties with the synergistic effects of the two material. For applications such as elevated temperature vulcanisates a sulphur/accelerator combination was incorporated for the introduction of sulphur cross links to the system apart from the most common zinc oxide cross links for vulcanisation of polychloroprene rubber.

The formulation with the carboxylated polychloroprene and the vinyl acrylic blend with dispersions of zinc oxide, antioxidant and alkyl phenolic resin with a dispersing agent and a biocide demonstrated very good bond strength for substrates such as wood to wood, veneer to veneer, formica to veneer and leather cloth to veneer. The bond strength for applications such as rubber to rubber and rubber to leather were below expectation.

Further research could be carried out with different types of polychloroprene latex, different blends of polychloroprene latex with other elastomers, different vinyl acrylic blends and different types of resins in the formulation to improve the bond strength for laminates such as rubber to rubber and leather to rubber other applications.

XIII