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IMPROVEMENTS IN PERFORMANCE OF POLYCHLOROPRENE RUBBER BASED ADHESIVES

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ABSTRACT

Polychloroprene rubber (CR) has been used for decades as the base polymer in rubber based adhesive applications: for example in the construction, furniture and upholstery industries. The conventional method of preparing the polychloroprene polymer for formulating and milling with other critical ingredients and then presenting final adhesives for applications has been in solvent diluted fluids.

Even though polychloroprene is well known as the balanced material in rubber adhesives, adherends such as plasticiser incorporated synthetic leathers, Ethylene vinyl acetate co-polymer cannot be adhered by CR only. A graft polymer of MMA with CR could be widely used because of its plasticizer resistance.

This paper presents the current progress and technology of a grafting procedure to formulate adhesives, using solvent based polychloroprene grades. The technology for CR grade adhesive applications is described along with comparisons with different chemical ingredients and solvent systems.

Key words: grafting, polychloroprene rubber, solvent base, synthetic leather

INTRODUCTION

The history of adhesives has been well documented. Early glues were based on naturally occurring substances such as animal fats, casein and vegetable extracts. It wasn't until the 1940s and 50s and the development of synthetic polymers that advances were made to produce reliable and controllable "adhesives". This was the start of adhesives and adhesion.

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The term, adhesive, covers a multitude of different chemical compositions, which all ultimately form a polymeric material to join and hold together two surfaces (Reilly, 1990). Adhesives can be subdivided into a number of different chemical types, each with their own characteristic cure mechanisms.

Polychloroprene (Neoprene) rubber has been used for decades as the base polymer for a number of adhesive applications, for example in the construction, furniture and consumer product industries. Neoprene is prominent among elastomers for adhesives because of its combination of polarity and crystallinity. The polarity gives a greater versatility in bonding a wide range of substrates and the crystallinity gives improved strength.

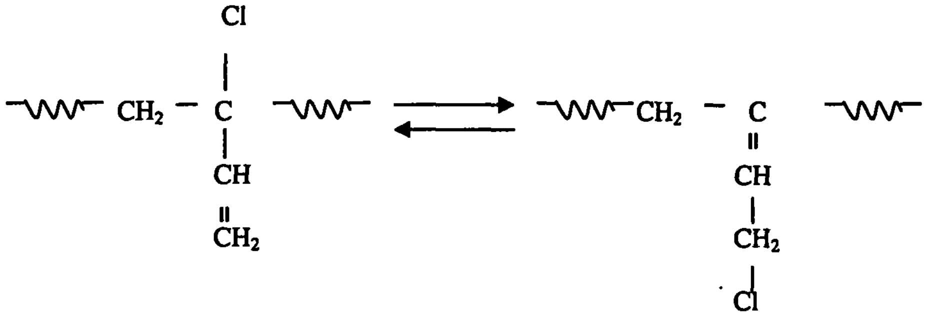
Polychloroprene manufacturers produce special grades of Polychloroprene Rubber (CR) for the manufacture of adhesives. Neoprene AD is such a grade. Neoprene adhesives are widely used in the footwear and furniture industries. They can be used to bond rubbers, wood, leather, plastics and even glass. It is leading among other adhesives due to its high bond strength and fast setting action (Skyprene, 1997).

The present study was undertaken to prepare various Neoprene graft grade AD adhesives, compare and contrast their adhesive bond strengths and thereby to develop a better adhesive based on presently available commercial grade Neoprene AD rubber adhesive. For this purpose, we have used two methods to increase the adhesive bond strength of Neoprene AD (Windspear, 1968).

Compounding and curing of Neoprene graft grade AD to increase the strength of adhesive bond

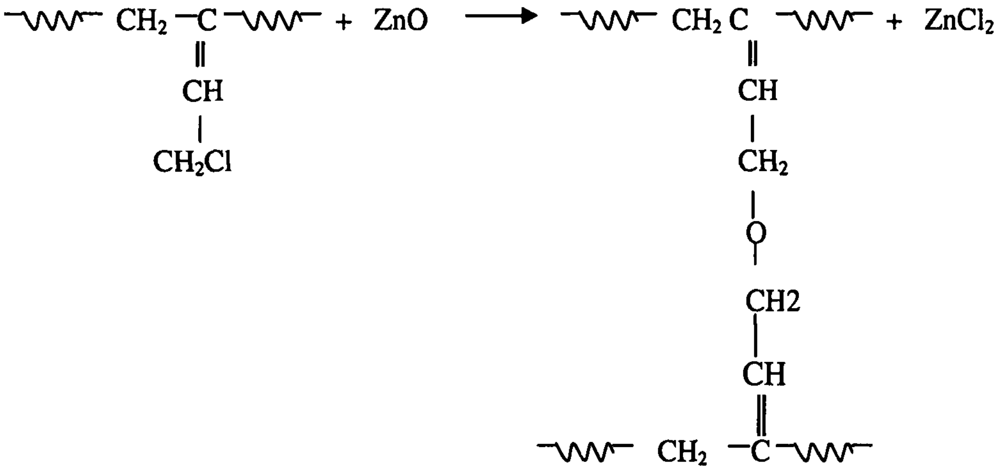
The vulcanization of Neoprene polymers is dependent upon the presence of metallic oxides, ZnO and MgO. The principal curing site is at the location of the 1,2 addition configuration of the monomer unit in the polymer chain. This cross-linking site occurs relatively along the linear chain. The Chlorine in the 1,2-addition configuration is allylic and accordingly labile.

The following equilibrium reaction probably exists and is the first step in the vulcanization of Neoprene (Windspear, 1968).



$$\sim CH_2-\overset{Cl}{\underset{CH=CH_2}{C}}\sim \;\rightleftharpoons\; \sim CH_2-\underset{CH-CH_2-Cl}{\overset{}{C}}\sim$$

Zinc oxide is believed to be directly involved in the cross-linking reaction. The role-played by ZnO in the curing reaction can be illustrated using following mechanism.



Ether linkages are formed between two molecules through the tertiary allylic chloride.

$ZnCl_2$ formed is an active catalyst of vulcanization. Unless it can be scavenged, its presence during processing operation can cause scorching problems.

Action of MgO as a stabilizer (Windpear, 1968)

$$2ZnCl_2 + MgO \xrightarrow{H_2O} 2\,Zn(OH)Cl + MgCl_2$$

Magnesium oxide function in the Neoprene vulcanization is to scavenge chloride ions resulting from the cross-linking reaction. The degree and the rate at which it removes the by-product chloride ions from the field of action have a marked effect on the vulcanization process.

Therefore, the addition of ZnO and MgO increases the storage stability of the adhesive and stability of the bonds (Cowie, 1973).

Resins are added in compounding to improve the flow properties of rubber, to improve the physical properties, such as hardness and tensile strength and increase tack.

Petroleum solvents are added as softeners in preparing the adhesives. When these are added to rubber, the solvent molecules penetrate into rubber and lubricate the rubber molecules, causing plastcization. This is a physical action, which prevents the interaction of rubber molecules. Petroleum solvents also facilitate the incorporation of powdery fillers, uniformly in the rubber network.

Grafting MMA to Neoprene to increase the strength of adhesive bond

A graft polymer is a co-polymer comprised of a main backbone chain, to which side chains containing different atomic constituents are attached at various positions. The main chain may be either a homopolymer or a co-polymer (Cowie, 1973).

Grafting could be accomplished by activating the synthetic rubber polymer Neoprene and simultaneously grafting and co-polymerizing the methyl methacrylate monomer (Neoprene, 1996). The process involves the formation of free radical centers along the rubber molecules by the addition of an initiator. After polymerization, the graft rubber contains Neoprene having small number of relatively long side chains of MMA (Cowie, 1973).

Effect of tackifying resin on peel strength

The most important component in an adhesive formulation is the tackifying resin. The type and amount of resin can affect properties such as contactability, open time, bond strength, heat resistance and specific adhesion. The Glass transition temperature (Tg), softening point, polarity and compatibility of the resin with the polymer are all involved in determining its effect on adhesive properties. The most common resin types used with polychloroprene are alkyl phenolic resins, terpene phenolic resins, normally used hydrogenated rosin and rosin esters, coumarone indene resins and hydrocarbon resins. Resins are used at 20 – 60 parts per hundred parts of polymer.

An important function of the resin is to maximize interfacial bonding. Through its plasticizing effect, the resin facilitates polymer diffusion between the adhesive films on the substrate surfaces when they are brought into contact. Without this rapid interdiffusion bond strength development would be retarded and failure could occur along the adhesive substrate rather than bonding cohesively or within the substrate.

Resins also function to extend the open time, *i.e.* the length of time after the adhesive film has dried to the time when assembly of the substrates with sufficient, reliable bond strength is possible.

In many instances, improvement in one property by a particular resin comes at the expense of another. For example, high softening point resin may impart good hot bond strength to an adhesive and may also reduce contactability (Shields, 1976).

The experiments reported in this paper were focused on the effect of compounding and grafting and the effect of various resins and solvents on the adhesive property of commercially available grade of Neoprene AD.

Improvements in performance of polychloroprene rubber based adhesives

Peeling strength and adhesive bond strength were used as the inspection tool to investigate the adhesive properties of adhesive concerned. A bonded adhesive joint is gradually forced apart from the edges inward; the tearing of the adhesive, which occurs, is called peeling. The peeling strength after 24 hours of applying the adhesive is called the adhesive bond strength.

EXPERIMENTAL

Control sample

Fundamental properties of this Neoprene AD

Color	- milky white
Solution viscosity	- same as conventional Neoprene AD
Smell	- none
Processibility	- excellent
Shape	- chips
Crystallization rate	- very fast
Specific gravity	- 1.23
Storage stability	- good
Discoloration in Sunshine	- less than conventional Neoprene Type AD
Solubility	- easily soluble in usual Neoprene solvents

Procedure 1- Adhesive type 1

Materials

Neoprene AD
Solvent mixture
Toluene
Water
Petroleum Spirit
Ethyl Acetate

Following formulation was used to compound Neoprene AD

Ingredients	**Parts by weight**
Neoprene AD	150.0
Magnesium Oxide	6.0
Zinc Oxide	6.0
Phenol Formaldehyde Resin	60.0
Water	1.5
Ethyl acetate	250.0
Petroleum solvent	322.0
Toluene	130.0

Method

Mastication of Neoprene type AD was done by a two roll mill for 15 minutes. Zinc oxide & Magnesium oxide powder were added in the order to the masticated rubber and allowed to disperse well. After 20 minutes of milling, the batch was taken out and allowed to cool at room temperature.

Ethyl acetate, Petroleum solvents, Toluene and Water are mixed in the given proportions. Phenol formaldehyde resin in crystal form was also incorporated to the mixer. This was put on a shaker and kept idling for 16 hrs till sufficient swelling of the rubber has taken place.

On the following day the solution is stirred well for 15 minutes and the resulting solution was taken as the stock solution.

Procedure 2 - Adhesive type 2

Ethyl acetate, Petroleum solvent, Toluene and Water are mixed in the given proportions. Phenol formaldehyde resin in the crystal form was added to this mixture and about one half of the solvent mixture along with Neoprene Type AD was poured on. Zinc oxide and Magnesium oxide in the powdered form was dissolved in a small amount of the solvent mixture.

This mixture was kept idling on a shaker for 16 hrs till sufficient swelling of the rubber has taken place. On the following day, the solution was stirred well for 15 minutes using an internal mixture.

The remaining portion of solvent mixture was then added, stirred for another 15 minutes and the resulting solution was used as a stock solution.

Procedure 3 - Adhesive type 3 (grafted type)

Following materials and the formulation were used in the experiment

Materials

Neoprene AD
Solvent mixture
Methyl methacrylate
Toluene
Benzoyl peroxide

Following formulation was used to compound Neoprene AD

Ingredients	**Parts by weight**
Neoprne AD	50.0
Methyl methacrylate (MMA)	50.0
Benzoyl peroxide (BPO)	0.25
Toluene	275.0

Dissolved Neoprene type AD in Toluene in a 500 ml reaction vessel. Added MMA into this Toluene solution. Heated up the vessel to 80^0 C in a water bath. While reaction mixture was keeping at 80^0C added Toluene solution of BPO and continued agitation. After about 4 hrs, when the solution viscosity reaches the required level, cooled the vessel to room temperature.

Procedure 4 - Adhesive type 4 (Grafted type)

Following formulation was used to compound Neoprene AD

Ingredients	**Parts by weight**
Neoprene AD	50.0
Toluene	200.0
Methyl Ethyl ketone	86.0
MMA	60.0
BPO	0.2

Method

Neoprene, Toluene and MEK were added to a round bottom flask, fitted in a water bath at 30^0C. The temperature of the water bath was increased to 90^0C and the mixture was stirred for 2 hrs. MMA was added to the mixture and stirred for another 30 minutes. BPO mixture was added and reaction was continued for 2 hrs.

Effect of resins on peel strength of an adhesive

Trials were carried out using formulation and procedure used in the Adhesive Type 1 but varying the resin type and composition.

A mixture of Ethyl acetate, Toluene and Petroleum spirit was used as the solvent mixture.

Ingredients	**Parts by weight**
Neoprene AD	100.0
MgO	5.0
ZnO	5.0
Water	1.0
Ethyl acetate	167
Petroleum spirit	215
Toluene	87

Three different tests were performed varying the type and the amount of tackifying resin;

Test 1	Amount of PF resin was varied as 10, 20, 40 and 60 phr
Test 2	Amount of CI resin was varied as 10, 20, 40 and 60 phr
Test 3	Amount of Wood Rosin was varied as 10, 20, 40 and 60 phr

Effect of solvents on peel strength of adhesive

Trials were carried out using formulation and procedure used in the preparation of adhesive type 1 but varying the solvent mixture.

Solvent compositions	
MEK/Toluene	0 /100, 20 / 80, 70 / 30
MEK/toluene/Petroleum spirit	1 : 2 : 1
Ethyl acetate/Toluene/Petroleum spirit	1 : 2 : 1

Procedure for the determination of adhesive bond strength

Strips of approximately 150 × 25 × 3mm of compounded rubber was cut and the surface to be bonded were buffed using emery cloth. The surface of the samples were washed with 1,1,1-trichloroethane to remove any dirt or oil and allowed the strips to dry well. Applied a sufficient quantity of adhesive over an area of approximately 75 × 25 mm of the buffered surface of each strip as a thin uniform layer. When the surface was dried, another coat of adhesive was applied. When second adhesive coat is dried to a point where there is still a thickness but no tendency for the film to lift when tested with a finger, the sample was pressed with a 2kg hand roller. The samples were air dried for 24 hrs and the adhesive bond strength was measured using tension test machine. The maximum force during stripping at the speed of 25 mm/min was expressed as the adhesive bond strength.

RESULTS AND DISCUSSION

Comparison of adhesive bond strengths of the prepared adhesives

Instrument-Tensile Strength Machine (Instron type)

It is known that most adhesive manufacturing industries do not mill Magnesium oxide and Zinc oxide with Neoprene AD rubber to minimize the cost and due to lack of milling facilities in their laboratories. However, experiments carried out in this work show that this could lead to poor properties resulting in weak bond strengths of adhesive ultimately.

For example results obtained with milling and unmilling of Neoprene AD clearly show that the (cured rubber/ cured rubber) adhesive property is highest in the adhesive type 1 where Neoprene AD is milled with ZnO and MgO (Fig. 1).

Further, the adhesives made from milled Neoprene are smoother in texture and the dry ingredients are usually dispersed better. This could probably be due to milled Neoprene cement with smaller particle sizes consequently penetrating porous surfaces such as rubber and leather to a greater extent than an adhesive made from unmilled polymer. Therefore, they will have a greater adhesion to these surfaces.

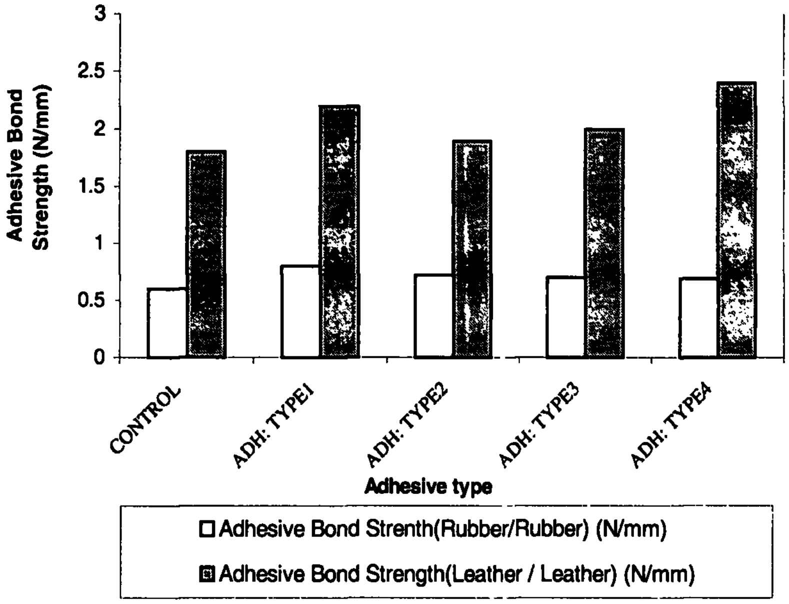


Fig. 1. Comparison of adhesive bond strength in rubber/rubber and leather/leather (N/mm)

Adhesive type 1 shows higher value for adhesive bond strength when compared to others for rubber to rubber adhesion (Fig. 1). However both grafted and compounded adhesives show higher bond strength when compared to the commercially available adhesive (control sample).

Both grafting procedures give similar bond strength for rubber adhesion and show an improvement when compared to the control sample. Grafting of polar materials to the rubber chain could be one effective way of increasing the bond strength.

The adhesive bond strength for leather material is higher than that of the control in all four types of adhesives. Adhesive bond strength increases by 25% for adhesive types 1 and 4, while slightly lower values were shown for adhesive type 2 and 3, when compared with the control.

However, no significant difference was observed between four types of adhesives prepared.

Effect of resin on bond strength

PF resin is found to be the best among the three resins (PF, CI, and WR). Bond strength is found to increase rapidly up to 40 phr (Fig. 2). After this limit the effect is rather slow. CI resin and WR are found to increase the bond strength up to 20-phr level. However, beyond this level bond strength is not much affected (Fig. 2.1 and 2.2)

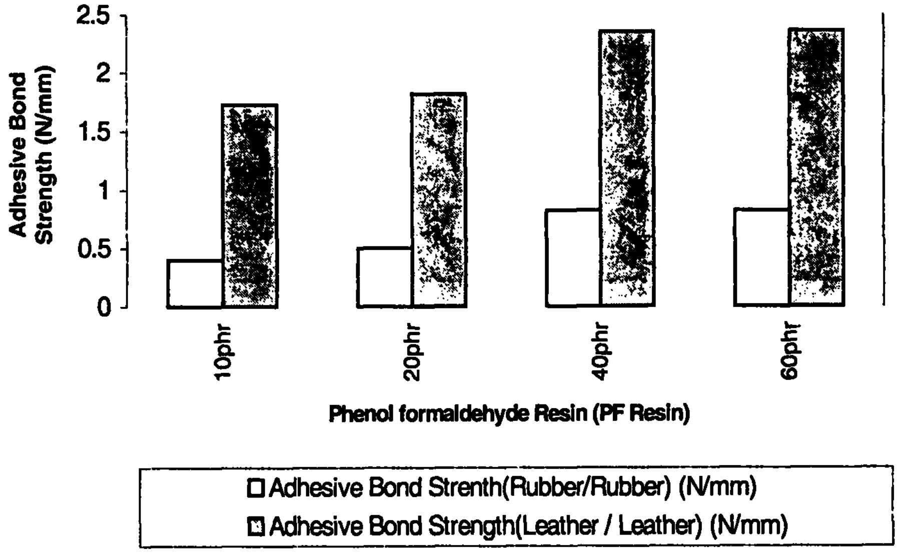


Fig. 2. Comparison of adhesive bond strength with different PF resin compositions

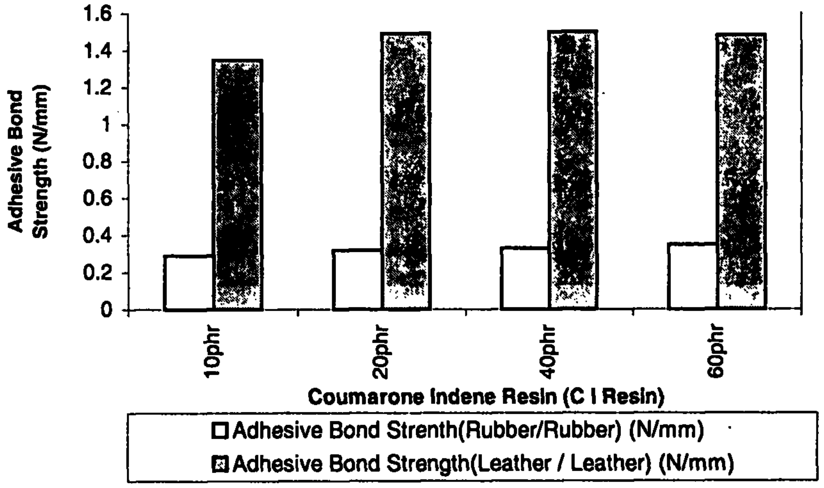


Fig. 2.1. Comparison of adhesive bond strength with different resin composition

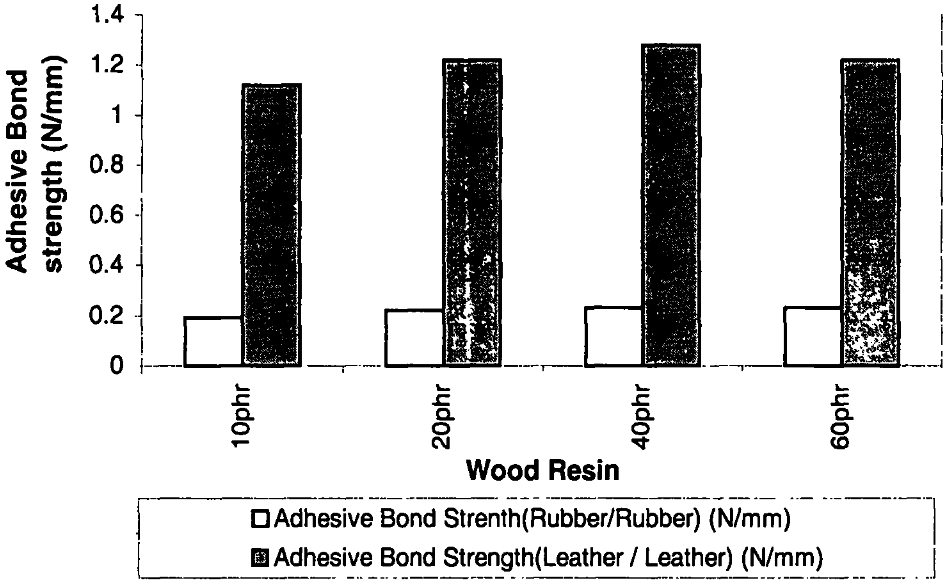


Fig.2.2. Comparison of adhesive bond strength with different WR composition

Resins seem to increase the adhesion strength up to an optimum level. Further increase of resin may increase the modulus of the adhesive component, resulting in shifting of the adhesion joints thus reducing the adhesion strength.

These resins could probably modify the rheology of the rubber by diffusing into the rubber so as to soften and enable it to coalesce more rapidly and to a greater extent, thus making it possible to form an adhesive bond when contacted with the surface. Yet, when attempts are made to break the bond, at the relatively high rates of stress, the adhesive has higher modules of elastic energy during bond rupture thus resulting in a high peel adhesion. The phenolic resin molecules could probably diffuse from one surface to another forming a hydrogen bonding network across the surface and thereby increasing the adhesive strength significantly (Shield,1976).

Effect of solvent on bond strength

From the above results, it could be observed that among the different solvents studied, solvent mixture of MEK/Toluene 70/30 offers the best overall performance. In a solution, the tough polymer becomes highly solvated and the extended polymer chain in a mobile form will dry to a coherent intermeshing polymer network. The solvent may also attack the substrate swelling or itching it so that its fusion with the adhesive is even more intimate. It is likely that the attack of solvent mixture MEK and Toluene in the ratio 70:30 on the substrate is more than that of other solvent (Fig. 3).

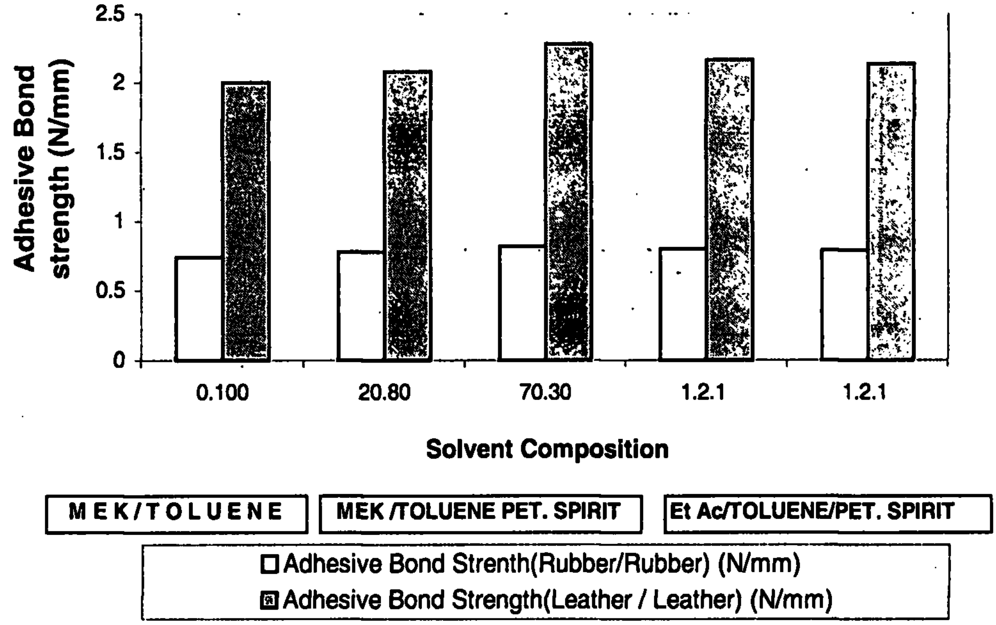


Fig. 3. Comparison of adhesive bond strength with different solvent composition

Problem in Neoprene cement is the deterioration of adherent possibly due to formation of hydrochloric acid by a slight decomposition of the chloroprene molecules. There is a high possibility that the formation of hydrochloric acid takes place at very slow rate at room temperature and heat or exposure to sunlight could catalyze this reaction. This deterioration could be prevented or inhibited by the presence of compounding ingredients such as Zinc oxide and Magnesium oxide. Apart from crosslinking rubber they could act as antiacids by neutralizing the acid (Windspear, 1968).

Finally, the results of the present work indicate that all four types of adhesives show improvement as adhesives for leather. Type 1 adhesive showed best performance in bonding rubber to rubber. However, a detailed study has to be conducted to check their storage stability and durability.

REFERENCES

Brown, R P (1979). Physical testing of rubbers. Applied Science Publishers Ltd, London. pp.305-315.

Cowie, J M G (1973). Chemistry and physics of modern materials. International Textbook Company Ltd. pp.99-120.

"Neoprene" (1996). Technical Bulletin. Du-Pont-Snowa Denko Co. Ltd. USA.

Reilly, C O (1990). Adhesives foe structural and engineering applications. Pergaman Press. New York. pp.1-25.

Shield, J (1976). Neoprene Adhesive. In: Handbook of Adhesives. Newnes-Butterworths Ltd, London. pp.174.

"**Skyprene**" (1997). Technical Bulletin. Rubber Division. TOSOH Corporation. Japan. 1-14 pp.

Windspear, G G (1968). Rubber Handbook. RT Vanderbilt Company. Inc, Newyork.. 119-129 pp.

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