SOME STUDIES ON THE ADHESIVE PROPERTIES OF CROSS-LINKED POLYVINYL ACETATE

A Thesis

Presented to the Ahmadu Bello University as partial fulfillment for the award of the Degree of Master of Science in the Faculty of Science,

BY

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To

My Wife,

Children, and my Mother.

(for their understandings, and to whom a lot is owed.)

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SYNOPSIS

Emulsion polymerisation method has been used to produce poly(vinyl acetate) samples in the presence of a cross-linking agent (divinyl benzene). The polymer is believed to be cross-linked as shown by the properties, although the extent of cross-linking is not known. The solid contents of the different samples were isolated and purified for use in the different experiments performed.

Studies have been conducted using films of the purified polymers cast from three solvents: Acetone/methanol mixture, benzene and chloroform. The tensile strengths of the films cast were measured on the Instron Tensile Testing machine. The results obtained showed that films from the same polymer product, but cast from different solvents have different tensile strengths. From this it was concluded that different interactions must have taken place between polymer and solvents. The films cast from acetone/methanol mixtures had the highest value of tensile strength and the least elongation-at-break value.

Adhesives of the different polymerisation products were made and used to bind metal substrates. The metals used in the tests were Aluminium, Zinc, and Titanium. The adhints were joined using the different adhesives and then dried for 72 hours at room temperature.

Measurements of the bond strengths of the metals were taken using the Instron tensile testing machine. From the analysis of results, it was found that poly(vinyl acetate) containing some cross-linkage bonded better. The results also show that beyond a certain extent of cross-linking in the polymer, bond strength decreases.

The total time the substrates were kept bonded before used for tests was kept constant at 72hrs. This period includes the times for heat-treatments. Results also show that heat-treatments of adhints would produce high bond strengths. The time of heat-treatment depends on type of plymer used, in terms of amount of cross-linking and time of polymerisation.

On plasticisation of the polymer samples with dibutyl phthalate (DBP), to 10% of polymer weight, the resultant products were used as adhesives. Comparison of results of bond strength of plasticised adhesives with those obtained for unheated substrates showed that plasticisation is not of advantage when bond strength is essential. This was found to be partially important when cross-linked polymers were used and substrates were titanium.

Emulsion poly(vinyl acetate) were found to be better adhesives with high bond strength when plasticised, and bonded adhints not heated. This was found to be general charateristics for the 8hr polymerisation emulsions.

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Mention must also be made of the followings who had contributed to the completion of this study in different ways:-

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C O N T E N T S

		Page
	Synopsis	i
1.0.	Chapter 1	1
1.1.	Objectives of the Present work	2
1.2.	General Characteristics of vinyl polymerisation	3
1.3.	Branching and Cross-linking in PVAc ...	6
1.3.1	Branching	6
1.3.2	Cross-linking	9
1.4	Methods of Polymerisation and their importance	11
1.4.1.	Bulk and Solution Polymerisation	11
1.4.2	Suspension Polymerisation	12
1.4.3	Emulsion Polymerisation	13
1.5	Characterization of Polyvinyl Acetate ...	16
1.6	Technological Importance and Uses of PVAc ...	18
1.6.1	Theories of Adhesion	19
1.6.2	Requirements for a Good Bond	21
1.6.3	Testing	22
	REFERENCES	24
	CHAPTER 2	27
	Experimental Methods	27
2.1.	Preparation of Polyvinyl Acetate (PVAc) ...	27
2.1.1	Materials and their purification	27

		Page
2.1.2.	Experimental	28
2.2	Preparation of Cross-linked PVAc using different amounts of cross-linking agents	29
2.2.1.	Materials and their purification ...	29
2.2.2.	Emulsion Polymerisation	30
2.3.	Isolation and Purification of Cross-linked PVAc	32
2.4.	Poly(vinyl acetate) films.	33
2.4.1.	Casting of the films	33
2.4.2.	Plasticization of Poly(vinyl acetate) ...	33
2.5.	Mechanical Testing of films	34
2.6.	Preparation and Testing of PVAc Adhesives	35
2.6.1.	Unplasticised adhesives	35
2.6.2.	Plasticised adhesives	35
2.6.3.	Unplasticised Emulsion adhesives ...	36
2.6.4.	Plasticised Emulsion adhesives	36
2.6.5.	Preparation of Substrates for Adhesive joints	37
2.6.5.1	Preparation of the metals	37
2.6.5.2	Preparation of Glass	38
2.6.5.3	Preparation of wood	38
2.6.5.4	Preparation of Cardboard	39
2.6.6.	Application of Adhesives and treatment of adhints	39
2.6.7.	Mechanical Testing for Tack	40

		Page
	REFERENCES	41
	DEFINITIONS OF SOME TERMS RELATING TO ADHESIVES AND MECHANICAL TESTING USED IN THIS WORK	42
	CHAPTER III.	43
	RESULTS AND DISCUSSIONS	43
3.1.	Dependence of Tensile Strength of PVAc on different Factors	43
3.1.1.	Effect of Solvents on Tensile Strength of PVAc films	43
3.1.2.	Interaction of acetone/methanol, benzene, and chloroform with PVAc.	45
3.1.3.	Effect of Plasticisation on the T.S. of PVAc films	46
3.1.4.	Dependence of Elongation on the Extent of Cross-linking in PVAc	49
3.2.	Bonding of metals substrates with PVAc ad adhesives (with or without cross-linking): Effect of heat treatment on tack ...	52
3.2.1.	Comparison of results for the two Substrates	57
3.3.	Comparative Study: Effect of plasticisation on Tack of heated and unheated bonded substrates	59
3.3.1.	Heated and unheated bonded Aluminium Substrates	60
3.3.2.	Heat-treated and untreated bonded Zinc Substrates	61
3.3.3.	Heat-treated and untreated bonded Titanium Substrates	63

		Page
3.3.4.	COMPARISON OF RESULTS FOR THE THREE ADHINTS	64
3.4.	Emulsion Adhesives of PVAc	66
	R E F E R E N C E S	70
	C O N C L U S I O N S	72
	T A B L E S	
2.1	... ...	31
2.2	... ...	31
3.2.1.	... ...	55
3.4.1.	... ...	69

CHAPTER I

1.0 INTRODUCTION

The adhesive art spreads over quite a large space of time. Carvings in the Thebes dating back to 3300 years were produced by gluing thin pieces of veneer to what appeared to be a plank of sycamore.[1] The modern usage and scope of the word "Adhesive" embraces quite a lot more than were called adhesives in the past. The early period limited the use of adhesives to naturally occuring products. In Crete, early use of wet-lime as binder for chalk, iron ocher, and copper blue frit pigments to walls had been recorded.[2] The Egyptian utilized gum Arabia from acacia tree, egg, glue, semi-liquid balsams and resins. Glues from fish, stag horns and soft cheese were also used for fixing wooden objects.[3] The very first adhesives which were in use for quite a long time were derived from vegetables, mineral substances, and animals, but they had little resistance to environmental conditions and therefore, gave way to the synthetic adhesives which are now given greater attention.

Except for the introduction of rubber and pyroxylin cements about a century ago,[2] there were little advancements in adhesive technology until the twentieth century. Within the last couple of decades, the natural adhesives have been improved and a large number of synthetic ones has emerged from laboratories.

The present day consumption of adhesives in different fields is so large, that there is an ever increasing demand for adhesives of different bond-strengths and purities. Many materials are now classified as adhesives, hence in broad terms, "an adhesive is a substance capable of holding materials together by surface attachment". Therefore, the term adhesive includes among others, cement, glue, mucilage, and paste.

Quite a large number of factors have been responsible for the growth of the adhesive industry. The march to produce new adhesive formulations is in the forward directions. and applications for these formulations are on the increase. Since there has not yet evolved a single all-purpose adhesive, (i.e. a "Master Adhesive"), laboratory efforts for improvements and creation continue. The field of adhesives is complex and fast-growing, offering challenges and rewards.

1.1. Objectives of the present work.

There are a number of publications covering the applications of poly (vinyl acetate).[4] One of the most important uses of (PVAc) poly(vinyl acetate) is in the formation of adhesives.

Most adhesives contain (PVAc) as a major portion, but other materials are usually also present to provide specific properties.

Because of the high commercial values of poly(vinyl acetate), most new findings in large laboratories and companies are kept as trade secrets, and patented, and therefore are not easily available, either to be subjected to tests of suitability, or to be used as basis for improvements.

The present work has been devoted, therefore, to synthesizing vinyl acetate polymer, at temperatures not higher than 60°C, to different degrees of cross-linking. Some of the adhesive properties of the polymers obtained would be studied and results compared with same properties tested for non-cross-linked poly(vinyl acetate) obtained under similar conditions. The effect of some common solvents for PVAc, on its tensile strength and tack would also be studied using the synthesized samples.

The function of plasticizers is to convert the hard and sometimes brittle poly(vinyl acetate) into flexible and pliable product. It is hoped that in this work, the effect of a plasticizer on the adhesive properties to be studied, and on film formation of the obtained polymers would be examined.

1.2. General Characteristics of vinyl polymerization.

The processes by which unsaturated monomers are converted to polymers of high molecular weight exhibit the characteristics of typical chain reactions.

They are readily susceptible to catalysis, photo-activation, and inhibition.[5] The following free radical chain mexanizm, proposed by Staudinger,[6] offers an explanation for the general characteristics of vinyl polymerizations.

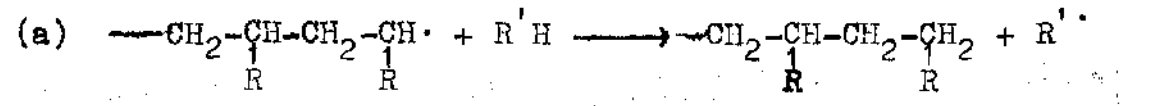
$$R\cdot \xrightarrow{CH_2 = CHX} R\text{-}CH_2\text{-}\underset{X}{\underset{|}{C}}H\cdot \xrightarrow{CH_2=CHX} R\text{-}CH_2\text{-}\underset{X}{\underset{|}{C}}H\text{-}CH_2\text{-}\underset{X}{\underset{|}{C}}H\cdot \quad (1\text{-}1)$$

$\longrightarrow$ etc.

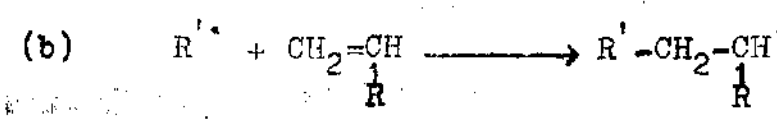
Where X is a substituent which may be C_6H_5, Cl, Br, $OCOCH_3$, $COOCH_3$, or H. The chain propagation step consists essentially of free radical attack at one of the double bonded carbon atoms of the monomer. One electron of the double bond pairs with the odd electron of the free radical to form a bond between the free radical and one carbon atom, the remaining electron of the double bond shifts to the other carbon atom, which then becomes a free radical. In this way, the active centre shifts uniquely to the newly added monomer, which is thereby rendered capable of adding another monomer.

The overall polymerization process involves at least two other steps:- chain initiation, which must depend on a reaction which introduces free radical into the system, and chain termination, whereby the terminal radical on a growing chain is destroyed or otherwise rendered inactive. A fourth step which is of importance in vinyl polymerization is the chain

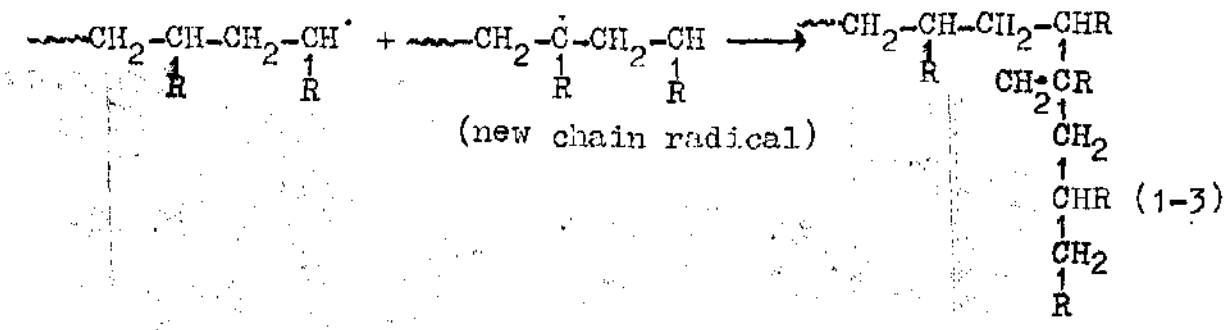
transfer, whereby the activity of the chain radical is transferred to the solvent, the polymer, the monomer, or a transfer agent, R'H.[7] Schematically presented as:-

(a) 

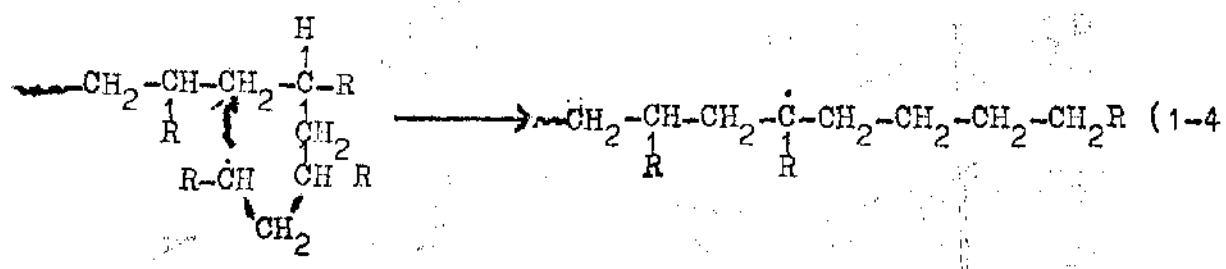
and

(b)  (1-2)

Branching results from transfer to polymer. Radicals may transfer intermolecularly resulting in long chain branching:-

 (1-3)

or intramolecularly, resulting in short chain branching:-

 (1-4)

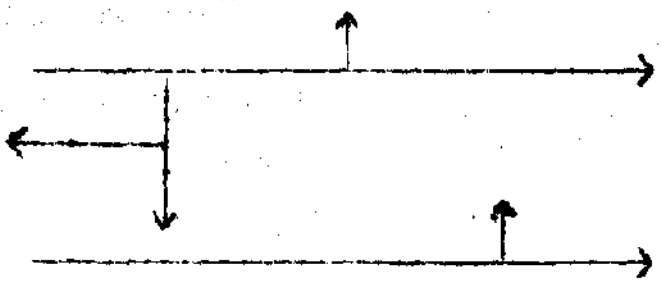
1.3 Branching and Cross-linking in Poly(vinyl acetate)

While linear chain structure is the rule among vinyl polymers the monotonous succession of bifunctional units may occasionally be interrupted by a unit of higher functionality. The frequency of incidence of such units along the chain depends on the monomer and conditions of its polymerization. Two common sources of non-linearity in vinyl polymerization are:- branching, resulting from chain transfer with monomer or polymer, and cross-linking in polymerization of diene or divinyl monomer.[8] It has become customary to differentiate the sources of non-linearity in diene polymers by the term "braching" and "cross-linking." It is also always pointed out that, whereas infinite network formation is a direct consequence of cross-linking, branching yeilds only finite molecules.

1.3.1. Branching

In a vinyl polymerization which is propagated by free radicals (1-2), a growing chain may occasionally enter into a chain transfer reaction with a polymer molecule. The growing chain is terminated and the reactivated polymer molecule proceeds to grow a new chain transfer. The resulting branched polymer molecule may sub-sequently undergo activation at another of its units, and another chain is added to the molecule at this point.

Repetition of this process a number of times may yeild highly branched molecules having a structural pattern like: in fig (1-5). The direction of each chain's growth is indicated by an arrow which also marks the point at which transfer terminates its growth.



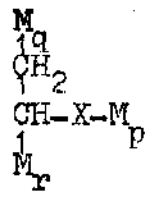
(1 - 5)

If chain transfer of the centre to a previously formed polymer molecule is followed ultimately by termination through coupling with another similarly transferred centre, the net result of these two processes is the combination of a pair of previously independent polymer molecules. If the chain transfer involves removal of an atom, (often hydrogen) from the monomer, the ensuing growth from the transfer radical will produce a polymer molecule bearing a terminal unit which retains its vinyl group. If then the point of attack is presumed to be in the substituent X, (see structure below), the sequence of reactions set off by chain transfer with the monomer may be represented as:-

$$M_p^{\cdot} + CH_2=\overset{X}{\underset{|}{C}}H \longrightarrow M_p-H + CH_2=\overset{X^{\cdot}}{\underset{|}{C}}H \xrightarrow{+M} \qquad (1\text{-}6)$$

$$\longrightarrow CH_2=CH-X-M_p$$

Another chain radical may acquire the terminal unit ofthe the molecule (1-6) in one of its propagation steps. This would mean that the terminal unsaturated unit may be incorporated as one of the units combined in another growing chain. When this occurs, a branched polymer is produced.[9]



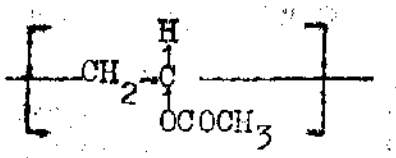
(1-7)

It should be noted that branching processes can not in itself generate an infinite network structure. It is to be expected therefore, that the branched polymers thus produced will remain soluble and fusible, in the absence of other processes.

Vinyl acetate has a transfer constant with the monomer, but that with the polymer unit is somewhat larger than for the the generality of other vinyl polymers.[10] For common polymers e.g. styrene, methyl methacrylate and methyl acrylate, the transfer constant is about 2×10^{-4} and for vinyl acetate, it is 8×10^{-4} (at $60^{o}C$).[8]

The methyl group of the acetyl radical appears to be the principal site of transfer, although in the polymer unit below, the tertiary hydrogen atom may make a large contribution, hence the non-linearity in poly(vinyl acetate) having degrees of

polymerization of several thousands or more can not be neglected



(1-8)

The average degree of branching increases with coversion, but formation of infinite networks seems impossible. Each chain transfer with a monomer molecule terminates the growth of a chain, but only those transfer monomers whose vinyl groups subsequently polymerize, yeild branches.

1.3.2. Cross-linking

Polymer molecules formed at the very beginning of a polymerization will be quite linear. But because they are exposed to attack by radicals of other growing chains over a large span of conversion, they have maximum opportunity to acquire cross-linking connections subsequent to their formations Those formed late in the process will contain more cross-linked units initially but will have little opportunity to acquire more.[8]

Non-linear addition polymers are readily obtained by copolymerizing a divinyl compound (e.g. divinyl benzene) with vinyl monomer. Products obtained exhibit the insolubility and other characteristics of space-network structure, and are entirely analogous structurally to the space-network polymer

produced by the condensation of polyfunctional compounds. Owing to the length of the chains in vinyl polymerizations, as little as 0.01% of the divinyl compound may be sufficient to bring about gelation. The space-network polymer formed was insoluble in liquids which would readily dissolve the polymer were it not for the net-work structure." The copolymerization of a small amount of divinyl benzene with styrene[12] offers the chance of introducing cross-linkages in a manner superficially analogous to that involved in the polymerization of a conjugated diene, but more amenable to control. The ethylenic group remaining in the divinyl unit after one of its vinyl groups has polymerized is approximately as susceptible to polymerization as it was initially.

The same arguments holding for cross-linking of styrene could be assumed to hold for vinyl acetate. Copolymerizing vinyl acetate with a small quantity of divinyl benzene might lead to the formation of an infinite network. The product could be insoluble in conventional solvents if polymerization was in the presence large amounts of divinyl benzene and was allowed to proceed for a reasonably long period.

1.4. Methods of Polymerization and their importance.

Vinyl acetate is polymerized by the free-radical addition reaction, as described in 1.2. Free-radical generated by decomposition of organic peroxides such as benzoyl or hydrogen peroxide or of organic "per" salts such as potassium or ammonium persulphate are commonly used to initiate the polymerization. Methods used are bulk, solution, suspension, and emulsion polymerization of the vinyl acetate monomer. Reactions are carried out usually at temperature significantly above the glass transition temperature Tg of Polyvinyl acetate (about 28°C).

1.4 1 Bulk and Solution Polymerization.

Bulk polymerization of vinyl acetate is not very popular. The difficulty of removing the heat of polymerization, and of controlling the polymerization reaction and the occurrence of branching at high polymer-to-monomer ratios, which leads to insolubilization, have made bulk polymerization unattractive.[13] The mechanism and kinetics of bulk and solution polymerisation are very similar. The solution polymerization mechanism is mainly determined by the type of initiation used. (free-radical and cationic initiation, heat and ultraviolet radiation) and by the type of solvent employed. The solvent often influences the final molecular weight and the nature of the polymer end groups.

The solvent could also determine the degree of stereoregularity of the resulting polymer, as in the case of polyvinyl chloride, though no such solvent effect has been noted with vinyl acetate.[14] Finally, a solvent that dissolves the monomeric vinyl acetate but not the polymer, such as an aliphatic hydrocarbon, will bring about a heterogeneous polymerization by precipitating the polymer as soon as it is formed. For solution polymerization, effect of each solvent to be used should be properly understood before embarking on the experiment. e.g. benzene, even in small quantity, reduces the rate of polymerization of vinyl acetate appreciably.[15] The order of reaction is rather complex, changing constantly as the monomer concentration increases. However, in methanol, Yano and Matsumoto[16] found that the rate of polymerization of vinyl acetate was not influenced by various ratios of methonol, and vinyl acetate but that the degree of polymerization increased as the vinyl acetate concentration increased.

1.4.2. Suspension Polymerization.

Suspension polymerization of vinyl acetate is an important industrial process. Numerous patents, however, deal with the vinyl acetate suspension polymerization, mainly describing various protective colloids and catalysts.[17] It has been recognized long ago, although never really proven, that Kinetically, the suspension polymerization is a "water coded

bulk polymerization."[18] The particles that are formed during suspension polymerization are usually spherically shaped. Small amounts of protective water-soluble colloids are used, to prevent particles from coalescing, examples are polyvinyl alcohol, gelatin, maleic anhydride - vinyl alkyl ether copolymer.

1.4.3. Emulsion Polymerization.

The emulsion polymerization process is most important both in the laboratory and commercial production of polyvinyl acetate, the suspension, solution and bulk polymerization following in that order of importance. However, the emulsion polymerization process of vinyl acetate is also the least understood. Emulsion polymerization recipes may consist of: vinyl acetate 80 to 100 parts: water 80 - to 100 parts, emulsifier 2 to 6 parts, initiator 0.5 to 1.5 parts. The common emulsifiers for emulsion polymerization of vinyl acetate include polymers, like polyvinyl alcohol, hydroxyethyl cellulose, gum arabic: anionics such as sodium lauryl sulphate, alkyl aryl sulphonates, and nonionics like polyethylene oxide alkyl phenols, and fatty acid ethers. The commonly used initiators include ammonium persulphate, potassium persulphate, hydrogen peroxide, water-soluble azo compounds such as 2,2'-azobis (2-methyl-4-carboxybutyronitrile).

The Smith-Ewart theory[19] is based on work done by Harkins[20] stating that essentially, an emulsion polymerization consists of a system of water, a monomer that is water-insoluble, an emulsifier, and a water-soluble initiator, which produces radicals when decoposing. The emulsifier forms micelles, (about 10^{18} cm^{-3}), solubilizing monomer, which is transported by diffusion through the water phase from monomer droplet into emulsifier micelle. The free radicals formed from the decomposition of initiator diffuse into the miscelles and start the polymerization. Since micelles are more in number than monomer droplets, the polymerization takes place essentially only in the micelle and not in the monomer droplets. Monomer in micelle is used up rapidly, new monomer then diffuses into micelle, which is now swollen with polymer, until the monomer droplet disappears and the micelles have changed to polymer particles. No new micelles can be formed after a certain time, because the total surface are of the particles in the system increases, and thus the emulsifier concentration in the acqueous phase is reduced to below the critical micelle concentration for the surfactant. This occurs at about 15 - 20% conversion.

Smith and Ewart proposed three different cases for the polymerization occuring in the polymer-monomer particle, as follows:-

Case I. The rate of entry of radicals into the micelle containing monomer is low, but the rate of exit is high. This case is highly improbable, because a polymeric radical will not diffuse out of particle faster than a small one will enter.

Case 2. The rate of exit or termination of radical is much slower than the rate of entry. In this case, the rate if polymerization can be described by the expression

$Rp = Kp(M)(Kd\ If/Kt)^{\frac{1}{2}}$ where

Rp = rate of chain propagation

Kp = propagation constant

(M) = monomer concentration

Kd = decomposition constant

(I) = initiator concentration

f = initiator efficiency

Kt = termination constant.

Case 3. The rate of termination is much faster than rate of entry or of exit. Therefore, at any given time, the micelle particle would have one growing radical or none. The rate of polymerization is then described by the propagation step in any polymerization:

$dM/at = Rp = Kp\ (M)\ (R\cdot)$ where

$(R^{\cdot})$ = radical concentration.

One of the important points of this rate equation is the fact that an increase in initiator concentration does not lead to an increase in the rate of polymerization, though it would affect the molecular weight of the polymer.

The Smith - Ewart theory has certain limitations. Newer theories[21] argue that monomers such as methyl methacrylate, vinyl acetate, n-butyl methacrylate, vinyl chloride and styrene, which differ widely in water solubility, showed the same dependence of rate and particle number on emulsifier, initiator, and monomer concentrations over most of the range of variables studied. Brodnyan and co-workers[22] found that the rate of polymerization obeyed equation $Rp = (E)^{0.5}\ (I)^{0.5}$ and the number of particles obeyed the equation:-

$$Nw = (E)^{3.0}\ (I)^{0.0}(M)^{0.0}$$

where (E) = concentration of emulsifier in g/cm^3.

1.5. Characterization of Polyvinyl Acetate.

Polyvinyl acetate is a thermoplastic, odourless, tasteless, nontoxic, essentially clear and colourless resin. It has a noncrystalline structure. Most grades of the resin have a somewhat broad molecular weight distribution, and do not melt sharply, but soften over a temperature range. Polyvinyl acetate is neutral and noncorrosive. The various grades have good heat stability below 100°C, but show slight discolouration at about 150°C.

In the commercial world, the different molecular weight resins are conviniently graded by a viscosity number. (V.). Most of the differences in physical properties among polyvinyl acetate grades are primarily a function of molecular weight. All grades have good adhesion to many surfaces. The excellent adhesion is due in part to the highly polar acetate groups in the polymer and partially to the unique combination of viscosity, tack, tensile strength, and other properties existing during the application, formation of bond, and aging of bond.[23]

Emulsion polymerization products are divided into two groups[24]. The first type is made of fine-particle size, (0.1 - 0.2μ); polyvinyl acetate without protective colloid, but only with anionic or nonionic surfactants. The second, a larg-particle size (0.5 - 3.0μ) emulsion, which is often stabilized by protective colloid.[24] In the industry, most manufacturers specify properties of their emulsions to describe the polyvinyl acetate produced in their factories. These properties include:- particle size, molecular weight, (usually as high, medium, or low), film properties such as clarity, water and grease resistance, and tolerance of emulsions to various organic and inorganic chemicals. Other special tests may be necessary to characterize an emulsion polymer more thoroughly.

These are:- surface tension, heat, storage and compounding stabilities, solubility of resin in various solvents, compatibility of the emulsions with:- plasticizers, thickening agents; tensile strength, hardness and other film properties, and rheological behaviour.[23]

1.6. Technological importance and Uses of Polyvinyl Acetate.

Poly(vinyl acetate) PVAc) has found a very wide use in the adhesive industries. To select an adhesive, the time of setting, temperature, pressure and other relevant factors for best performance are considered. Poly(vinyl acetate) adhesives were adaptable to new high-speed machinery in the paper converting and packaging fields and were of importance as wood adhesives.[25] PVAc is now used in adhesives for book-binding, paper bags, milk cartons drinking straws, envelopes, multiwall shipping bags, automobile upholstery. leather binding, tile cements, and cigarette tips. This wide use is probably because of its relatively low cost, ready availability, and excellent adhesive characteristics. Its use in paint industry actually depends on its adhesive, binding and film properties. In textile industry, it is being used to impart durability and strength to woven cotton and other fabrics.[23]

1.6.1. Theories of Adhesion

The mechanism of adhesive attachments can still not be fully explained. There are now many theories that try to describe the phenomena of adhesion.[25]

a) Mechanical theory: Adhesion is described here, as a process whereby the adhesive flows, fills microcavities on the substrates, and on hardening, the substrate are held together mechanically. According to the mechanical theory, in order to function properly, the adhesive must penetrate the carvities on the surface of the adhints and displace the trapped air at the interface. While some adhesive applications can be explained by mechanical interlocking. it has been shown[26] that mechanical effects are not always of great importance.

b) Adsorption theory

The adsorption theory states that adhesion results from molecular contact between an adhesive and the adherend and the surface forces which develop. After intimate contact is achieved between adhesive and adherend through wetting, it is believed that permanent adhesion results primarily through forces of molecular attraction. Four general types of chemical bonds are recognised as being involved in adhesion and cohesion:- electrostatic, covalent, and metallic, which are referred to as primary bonds and van der Waals forces, which are refferred to as secondary bonds.

c) Electrostatic and diffusion theories[27]

The electrostatic theory states that electrostatic forces in the form of an electrical double layer are formed at the adhesive-adherend interface. These forces account for resistance to separation. This theory gathers support from the fact that electrical discharges have been noticed when an adhesive is peeled from a substrate.

The fundamental concept of diffusion theory is that adhesion arises through the inter diffusion of molecules in the adhesive and adherend. This theory is applicable only when both the adhesive and adherend are polymeric, having long-chain molecules capable of movement. The solvent or heat welding of thermoplastics is considered to be due to diffusion of molecules.

d) Weak-boundary-layer theory:

According to this theory, when bond failure seems to be at the interface, usually a cohesive break of a weak boundary
1 layer is the real event.[28] Weak boundary layers can originate from the adhesive or the adherend if any impurity concentrates near the bonding surface and forms a weak attachment to the substrate. Weak boundary layers formed from the bonding environment, generally air, are very common.

1.6.2. Requirements for a Good Bond:

The basic requirements for useful adhesive-bonded assemblies are cleanliness, wetting, solidification and proper choice of adhesive and joint design.[26]

Cleanliness:- To achieve an effective adhesive bond, a clean surface is the first requirement. Foreign materials such as dirt, oil, moisture, and weak oxide layers must be removed from the substrate surface, or else the adhesive will bond to the weak boundary layers, rather than the substrate in use. The removal of these foreign bodies generally involve physical, or chemical processes or a combination of the two.

Wetting:- The adhesive must "wet" the substrate while the adhesive is still in the liquid state. Wetting is understood as the spreading over and intimately contacting a solid surface by the adhesive. The result of good wetting is greater contact area between adherend and adhesive over which the force of adhesion may act.

Solidification:- The liquid adhesive, once applied, must be capable of conversion into a solid. The process of solidification of an adhesive could be achieved in three different ways:-

(1) Chemical reaction by any combination of heat, pressure, and curing agents.

(2) Cooling from a molten liquid to a solid.

(3) drying due to solvent evaporation.

The method by which solidification occurs depends on the choice of adhesive.

Adhesive Choice[29]

The general area of concern to the choice of an appropriate adhesive should be the material to be bonded, service requirements, production requirements and ease of access to obtaining the adhesive and the cost.

Joint design.

The adhesive joint should be designed to take advantage of the good properties of adhesives and to minimize their shortcomings. The maximum benefits of the adhesive can be obtained only in assemblies specially designed for adhesive bonding.

1.6.3. Testing.

When a good bond has been achieved, 1.6.2, the strength of the bond might need to be tested to estimate the ultimate use such bonded materials might be put into. The durability of adhesives in bonded joints is a function of stress and environment.[30]

The synthesized polymers (PVAc) are tested for their adhesive strength using the Instron testing machine.

The strength of bonding are expressed in Kg cm^{-2}. Preparation of adhints and application of adhesives to the surfaces of adhints, methods of curing and experimental usage of the Instron machine would be described under experimental methods.

Films cast from the different polymer samples, and in different solvents would be test for their tensile strength using the Instron machine. An account of the preparation of films, and steps for testing would also be given under experimental.

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CHAPTER II

EXPERIMENTAL METHODS

2.1. Preparation of Polyvinyl Acetate (PVAc).

2.1.1. Materials and their Purification.

1. Vinyl acetate stabilised with hydroquinone supplied by B.D.H. Chemicals Ltd. Poole, England.
2. Potassium persulphate, reagent grade.
3. Sodium persulphate, reagent grade.
4. Sodium Lauryl Sulphate, specially purified grade.
5. Sodium hydrogen orth-phosphate, hydrate, reagent grade.

The vinyl acetate monomer was purified by washing repeatedly with a 5% solution of Sodium hydroxide to remove the hydroquinone. Complete absence of yellow coloration in the Sodium hydroxide layer in a separating funnel, confirmed complete removal of the inhibitor. The purified vinyl acetate was washed with small portions of distilled water to remove traces of sodium hydroxide. (Cleanliness was confirmed using a Universal Indicator Paper, pH 7). The purified vinyl acetate was dried over dehydrated sodium sulphate, after which distillation was carried out. The fraction boiling off between 72°C and 72.5°C was collected and stored in a bottle and nitrogen

was bubbled into it before it was kept in a refridgerator, with the distillate used as soon as possible after collection.

Recrystallization of sodium and potassium persulphates were done in water. The crystals were dried in the vacuum oven and stored over silica gel in desiccators till required for use.

Sodium lauryl sulphate and sodium dihydrogen phosphates were used as supplied without further purification.

2.1.2. Experimental.

A 2-litre four-necked reaction kettle was fitted with a motor-controlled stirrer. The kettle was immersed in a constant temperature water-bath maintained at 60°C. After flushing the reaction kettle with nitrogen gas, and maintaining a nitrogen atmosphere in the kettle, 500cm^3 of freshly distilled water was introduced into the kettle. When the temperature of the kettle and its content was 60°C, the following reagents were introduced into the reaction kettle, with constant controlled speed of stirring:- 3g. of sodium lauryl sulphate, 3g. of sodium dihydrogen ortho-phosphate, and 4.5g. of recrystallized sodium persulphate. When the reagents had dissolved, 200g (214.8 cm^3) of purified vinyl acetate was introduced into the reaction mixture in the kettle, using a monomer dropper.

Polymerization was allowed to proceed for a total of 11 hrs with samples withdrawn at intervals using a 25cm^3 pipette. The polymer from some quantity of each sample that was withdrawn was isolated, purified and dried in vacuum oven.

2.2. Preparation of Cross-linked Poly(vinyl acetate) using different amount of cross-linking agents.

2.2.1 Materials and their purification.

1. All materials in section 2.1.1.
2. Di-vinyl benzene
3. Methanol - technical grade.

TTT The divinyl benzene, which had solidified due to long-time storage was broken into small pieces and put into a distillation flask. The flask was fitted with a 350°C quick-fit thermometer. By gradual heating, the fraction of p-divinyl benzene which distilled off at 199°C to 200°C was collected. (Boiling temperature of p-divinyl benzene being 199.5°C.)[1] The distillate was further purified by washing with a 5% solution of sodium hydroxide. Removal of stabilizer was assumed to be completed when the sodium hydroxide layer did not show any more red coloration. Distilled water was used in washing the purified divinyl benzene to remove excess base. The bright yellow liquid obtained, which floats on water, was decanted, dried over

anhydrous sodium sulphate, redistilled and finally kept in a refridgerator until it was required for use. Pure vinyl acetate, sodium and potassium per sulphate described in 2.1.1 were used. Methanol was used as supplied.

2.2.2. Emulsion Polymerization

The proceedure of polymerization was carried out as in 2.1.2.

Polymerizations to produce cross-linked poly(vinyl acetate) were carried out for periods of 11 hours for each concentration of the divinyl benzene used. The amounts of divinyl benzene used are shown in Table 2.1.

Samples were withdrawn from the reaction kettle at 2 hrs, 5 hrs, 8 hrs, and 11 hrs intervals after the start of each polymerization. 100cm^3 of each sample was precipitated to get the amounts of solids in them. (Table 2.2)

The remaining portion of the emulsion of each sample was kept in a closed sample-bottle for later use.

Table 2.1

Volume of D.V.B. in cm^3	% mole D.V.B. in Vinyl acetate-divinyl benzene monomer system
1.5	0.166
2.5	0.277
3.5	0.387
4.5	0.498
6.0	0.664
11.0	1.220

Table 2.2

Weights of Solid Poly(vinyl acetate) in $100cm^3$ of Emulsion in grams.				
	Time of polymerizations (hrs)			
	2	5	8	11
Amounts of D.V.B. in cm^3				
0	21.413	24.122	22.825	22.392
1.5	14.226	17.533	17.431	16.248
2.5	-	12.824	15.084	15.573
3.5	-	16.400	17.312	16.750
6.0	-	4.450	5.211	5.825
11.0	-	3.212	6.470	9.341

2.3. Isolation and Purification of Cross-linked Poly(vinyl acetate)

Precipitation of the samples prepared was carried out directly from the emulsions of each sample using a nonsolvent. The non-solvent used was a dilute solution of sodium chloride in water. The emulsion was added in drops to a large quantity of salt water with continuous stirring to prevent lumps from forming. The solid PVAc was filtered, using sintered glass funnel, and vacuum pump. The polymer was not allowed to go dry during filteration as this might cause lumping up. The filtered product was washed several times with freshly distilled water to remove salt, acid, soap, and any other impurities that was soluble in water. The pure solid poly(vinyl acetate) was transfered to large filter papers and left to dry in the open air for 12 hours. It was then transfered into a watch glass and dried in a vacuum oven at $35^{\circ}C$ over silica gel for another 12 hours. The products were weighed and again dried in vacuum oven until the weight was constant. It was stored in bottles kept in a desiccator until required for use.

2.4. Poly(vinyl acetate) films.

2.4.1 Casting of the films.

Solutions of the different samples of polymer were prepared using Chloroform, Benzene, and Mixture of acetone and methanol[2] (ratio 1:2.33) in turn.

One gramme of polymer was dissolved in 25cm^3 of each of the above named solvents. Each solution was homogenized by shaking the flask. Films were cast by gently pouring the 25cm^3 solution on to clean mercury surfaces kept in clean desiccators and placed in the fume cupboard. The solvent gradually evaporated. On complete evaporation, the films were removed from the mercury surfaces with a sharpedge. The films were kept on filter papers and kept in the constant humidity room, of RH of 25% and a temperature of 21^{o}C.

2.4.2. Plasticization of Poly(vinyl acetate)

To plasticize PVAc samples, the same solvents used in 2.4.1. were employed. One gram each of polymer sample was weighed and placed in cleaned, dry boiling tubes. 10cm^3 of solvent was added. A solution of the appropriate quantity of dibutyl phthalate (DBP) in the solvent, that would give 10% plasticizer based on polymer weight when 10cm^3 of the former were added was prepared. 10cm^3 of the plasticizer solution was added appropriately into each boiling tube.

Each of the boiling tube with content, was given manual shaking at intervals, till the polymer had dissolved into the solvent added.

The boiling tubes were then arranged into a mechanical shaker bath, maintained at $40^{o}C$. After 24 hours of constant shaking, the tubes with contents were removed from the shaker bath. $5cm^3$ of pure solvent was added to the contents of the tube to bring the volume to about $25cm^3$. After thorough shaking in bath for another 6 hours, the contents of each tube were poured on to clean mercury surfaces and films cast.

2.5 Mechanical Testing of films.

Strips measuring 4.5 x 0.7cm were cut out of the cast films. Using a micrometer-screw-guage, the average thickness of each strip was taken. The shear-load required to break each film strip was determined using the Instron machine (Model 1026). The gauge length of each strip was 3cm. The strain rate was kept constant at 100mm per minute, and measurements were carried out at constant humidy and temperature of 25% and $21.0^{o}C$ respectively. From the measurements taken, the tensile strength of each film sample was calculated using the formula:-

$$\text{Tensile Strength} = \frac{\text{Shear Load} \times 9.81}{\text{Width of film strip} \times \text{Thickness}} \quad NM^{-2}$$

The lengths, widths and thicknesses of the film strips were converted to unit of meter. Shear loads were expressed in killogramms.

Using the gauge length, cross-head speed chart speed and the actual chart movement, the elongation at break of each was also calculated using the formula:-

$$E\ \text{Elongation}\ (\%) = 100 \times \frac{\text{Actual chart extention}}{\text{Gauge length}} \times \frac{\text{Cross head Speed}}{\text{Chart Speed}}$$

2.6. Preparation and Testing of Poly(vinyl acetate) Adhesives.

2.6.1. Unplasticised adhesives.

Adhesives of different polymer samples were prepared by dissolving 1.0g of each polymer sample separately in 10cm^3 of chloroform in 50cm^3 conical flask. After 24 hours with periodic shaking of the flasks the contents of each flask were thoroughly stirred using a stirring rod. Where the solutions were very viscous, 5cm^3 of solvent was added to each flask and thorough mixing was done. In the same way, adhesives of polymer samples were again prepared using Benzene, and a mixture of acetone with methanol (1:2.33) ($^{v}/_{v}$)[2], respectively.

2.6.2. Plasticised adhesives.

Same quantities of polymer samples as used in 2.6.1. were used. The samples were each placed in boiling tubes. A solution of the appropriate quantity of DBP in the solvent that would give 10% plasticizer based on polymer weight when 10cm^3 of the

former were added was prepared. 10cm^3 of the plasticizer solution was added appropriately into each boiling tube and further treatments were as in 2.4.2.

2.6.3. Unplasticized Emulsion adhesives.

Using calculation of polymer content in a unit volume of emulsion, specific volumes were measured that would contain about 1g of poly(vinyl acetate) of each emulsion sample. These were put into different 50cm^3 conical flasks. Thickening of the emulsion solution was done by gradual evaporation, by placing the flasks in hot water temperature 50^{o}C. The obtained concentrated solution was used as adhesive.

2.6.4. Plasticized Emulsion adhesives.

Calculated volumes, based on polymeric content in emulsion solutions, of the different samples were placed in different boiling tubes, and concentrated where necessary. 5cm^3 of solutions of chloroform, methanol/Acetone mixture. and benzene, each containing appropriate quantity of DBP in the solution that would give 10% plasticizer based on polymer weight was added appropriately to the contents of the boiling tube. The tubes were arranged into a mechanical shaker bath, operating at 40^{o}C. The tubes were removed after 24 hours of constant rocking in the bath, and the contents used for adhesive tests.

2.6.5. Preparation of Substrates for Adhesive joints.

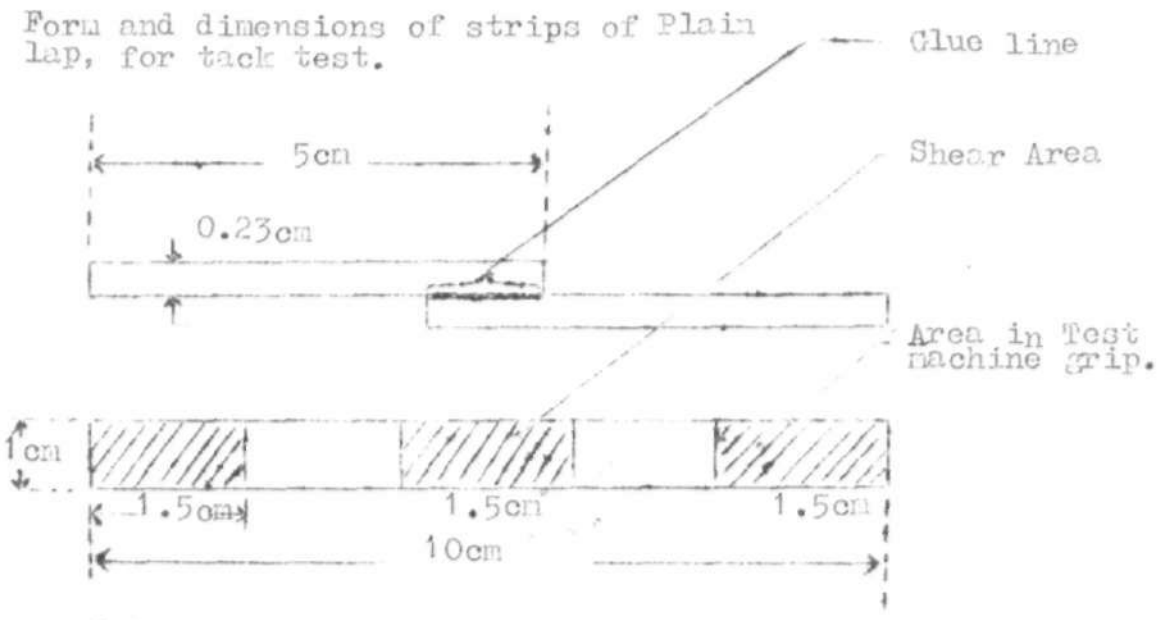
In studying the durability of adhints' bonds, the processing involved in obtaining superior durable bonds has been found to be of major importance.[7] Treatments given to the adhints in this work were according to specifications for treatments of adhints.[8]

2.6.5.1. Preparation of the Metals.

Metals used were Aluminum, Zinc and Titanium foils. The metals were cut into strips 5 x 1 cm. The strips were all soaked in warm water. The surfaces of the Aluminum and Zinc Strips were cleaned with dilute hydrochloric acid, after which they were again put into hot water. The strips of Aluminium, Zinc, and Titanium were all scrubbed with commercial "Vim." They were again washed in warm distilled water and dried. An area of (1.5 x 1) cm^2 was marked on one face of each strip. These marked areas at one end of the strips were sand-papered with 100 grit emery cloth. The sand-papered ends were cleaned using methanol. All the strips were then put into a flask fitted with reflux condenser containing purified toluene, and boiled for 30 minutes for degreasing. They were then dried and stored over silica gel in a desiccator until used.

(Fig. 2.1.)

Form and dimensions of strips of Plain lap, for tack test.



2.6.5.2. Preparation of Glass

Non-corrosive microscope slides were used. Strips 5 x 1 cm were cut, and an area (1.5 x 1) cm^2 etched from one end of each strip. The marked areas were sand-papered and cleaned with a piece of cloth, dipped in purified toluene. Storage was done over silica gel in evacuated desiccator until used.

2.6.5.3. Preparation of Wood.

Single ply of plywood supplied by the Epe plywood Industry, Epe Nigeria was used. The plywood sheet was sand-papered in the direction of the grain, after which strips measuring 5 x 1 cm were cut. An area (1.5 x 1) cm^2 was marked out on one end of each strip. The surfaces of the strips were cleaned for use by wiping them with a piece of cloth dipped in toluene. Storage was over silica gel in desiccator before use.

2.6.5.4. Preparation of Cardboard.

Card-board papers were also cut into strips with dimensions as in other reported adhints. The surfaces were wiped with methanol/acetone mixture and allowed to dry before storage. They were stored over silica gel in desiccator until they were used.

2.6.6. Application of Adhesives and treatment of adhints.

The sand-papered, cleaned and stored adhints were laid on filter papers with the etched surfaces up. Using a stirring rod, the content of each container in which adhesives had been prepared were again thoroughly mixed. The adhesive was then spread on the marked-out areas on each strip.

The adhesive was allowed to dry then, the adhints were joined using hand-pressure to remove any trapped air bubbles. Eight joints were prepared for each adhesive formulation. All the lap joints were placed under a constant load of 10kg for 30 minutes to ensure proper face contact, and complete exclusion of air bubbles. The adhints of each adhesive composition were then divided into two portions and given different treatments.

a) Air treatment:- In this treatment, the adhints were laid on filter papers on a flat surface to dry in the air for 48 hours. After the expiration of the drying time, measurements, of length and width of the contact areas were taken. The lap joints were then tested for tack using the Instron machine.

b) Heat-treatments. Here, the adhints that were not used for air treatment were put in the oven maintained at 100°C. The time of heat-treatment varied from 1 hour to 5 hours. After the expiration of the set time, the substrates were removed from the oven and allowed to dry in the open air at room temperature for the remaining time that would make the joining time add up to 48 hours. Measurements of length and width of areas in contact were taken and test for tack conducted.

2.6.7. Mechanical Testing for Tack.

The Instron Tensile testing machine (model 1026) was used in testing the bond strengths of adhints prepared with different samples of adhesive. The load cell 1026 CM with maximum load of 50kg was used in tests for tack. The strain rate was kept constant at 100mm per minute, and measurements were carried out at RH. 25% and temperature of 21°C. From the Curves obtained in the test, the tack was calculated using the formula:-

$$\text{Tack} = \frac{\text{Load}}{\text{Area of bonding}} \quad \text{Kg cm}^{-2}$$

where load = force of separation of adhints.

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DEFINITIONS OF TERMS RELATING TO ADHESIVE AND MECHANICAL TESTING* USED IN THIS WORK.

ADHERE	To cause two surfaces to be held together by adhesion.
ADHEREND	A body which is held to another body by an adhesive.
ADHESIVE	A substance capable of holding materials together by surface attachment.
ADHINT	An adhesive joint
BOND	The union of materials by adhesives.
BOND STRENGTH	The unit load applied in tension, compression, flexure, peel, impact, cleavage or shear, required to break adhesive assembly with failure occuring in or near the plane of the bond.
JOINT, LAP	A joint made by placing one adherend partly over another and bonding together the overlapped portions.
SUBSTRATE	A material upon the surface of which an adhesive containing substance has been spread for any purpose, such as bonding or coating. A broader term than adherend.
TACK	The property of an adhesive that enables it to form a bond of measurable strength immediately after adhesive and adherend are brought into contact under low pressure.
WETTING	Ability to adhere to a surface immediately upon contact.

*ASTM Designation: D907-60 Published through courtesy of American Society for Testing Materials. 1916 Race St, Philadelphia, Pa.

CHAPTER III

RESULTS AND DISCUSSION

3.1. Dependence of Tensile Strength of PVAc on different Factors

Figures (3-1), (3-2), (3-3), represent plots of Tensile strengths of films of Poly(vinyl acetate) produced at 5 hours, 8 hours, and 11 hours. Polymerisation, cast from different solvents (acetone/methanol mixture), benzene, and chloroform and containing different amounts of divinyl benzene (DVB) for cross-linking. The divinyl benzene in monomer mixtures for cross-linking was calculated as a percentage of the molar weights of the monomers in the mixtures for polymerisation.

3.1.1. Effect of Solvents on Tensile Strength of PVAc films

Fig. (3-1) represents the results of tensile strength (T.S.) for films cast from different solvents. Polymer samples used (cross-linked and uncross-linked), were recovered after five hours polymerization, and their T.S. were measured in the film form. The curves obtained show an initial rapid increase in tensile strength with extent of cross-linking, i.e. % DVB in bath. The tensile strength reaching different maximum values, which depend on the percentage DVB in monomer mixtures, finally decreases. The peak value of T.S. is highest in acetone/methano mixture, and is at 0.17% DVB in the polymerisation bath.

For films cast from benzene, the behaviour of T.S. with % DVB content is similar to that from acetone/methanol, except that the peak value of T.S. is lower. For films cast from chloroform, the initial increase in T.S. is gradual up to about 0.1% cross-linking agent in the bath, when it rises steeply to a maximum value at about 0.28% cross-linking agent in the Polymerisation bath. From there on it decreases.

The film from the 8 hours polymerisation product cast from acetone/methanol also has its peak T.S. value for the 0.17% DVB in bath, fig 3-2, and decreases in value through 0.28% to 0.39% DVB. The lowest value is obtained from the samples with no cross-linking agent. For films of the same samples cast from benzene, the peak T.S. value is also for the 0.17% DVB in bath. The pattern of variation of T.S. with % DVB in bath is the same as in fig. 3-1. The lowest T.S. value is observed for the sample of 0.39% cross-linking agent. For films cast from chloroform, T.S. decreases with increase in % DVB in bath to a minimum value at about 0.3% DVB in bath and increases thereafter.

The results of the tests performed on the polymer products of 11 hours polymerisation and different % DVB in monomer mixtures are shown in fig 3-3. For the unplasticised films, the tensile strength increases with cross-linking, rapidly at first, gets to a maximum and then decreases. For films cast from acetone/ methanol, or benzene, T.S. has a maximum value at about 0.23%

DVB in bath, and for those cast from chloroform, the products of 0.17% DVB in bath have the highest T.S. values. The tensile strength has the highest value for films cast from acetone/ methanol mixture and lowest value for those cast from chloroform.

For the three sets of results i.e. figs. (3-1, 3-2 and 3-3), the films cast from acetone/methanol mixture exhibit the highest T.S. followed by those cast from benzene. Those cast from chloroform can be seen to have, sometimes, much lower values of T.S. than those from the other two solvents or solvent mixture. Furthermore, for films cast from acetone/methanol or benzene, the film of highest T.S. corresponds to the % DVB in monomer mixture, whereas for those cast from chloroform the position of the highest value of T.S. (in terms of % DVB in bath), depends on the hour of polymerisation of the product.

3.1.2. Interaction of acetone/methanol, benzene, and chloroform with PVAc.

The results reported in 3.1.1. can be explained in terms of some specific or non-specific interactions of the solvents with PVAc.[1] Acetone/methanol being strongly capable of hydrogen bonding, would most likely give surface protection to PVAc. films by way of forming hydrogen bonds.[2] This protection would at least lead to a reinforcement of the film and hence disallow the polymer molecules from moving past one another. (slippage of chains). Consequently, a hard and brittle polymer film would result.[1,2]

For chloroform, the fact that the solubility parameters of chloroform (9.3) and PVAc (9.4) are very close,[1] the polymer would very easily dissolve in the solvent and the molecules of the solvent easily would lodge in-between the polymer chain molecules and weaken the polymer-polymer bondage.[1] When the polymer-polymer bondage is weakened, this in turn is manifested in the reduction of the T.S. of the polymer.

Benzene is classified as a polar aceptor,[1,3] hence its bonding to PVAc will be of some considerable strength, and at least stronger than the bonding between chloroform and PVAc. Benzene will likely have a bond, of either cation solvation or anion solvation with the polymer when dissolved in it,[3] therefore the films from benzene show larger tensile strength than those from chloroform.

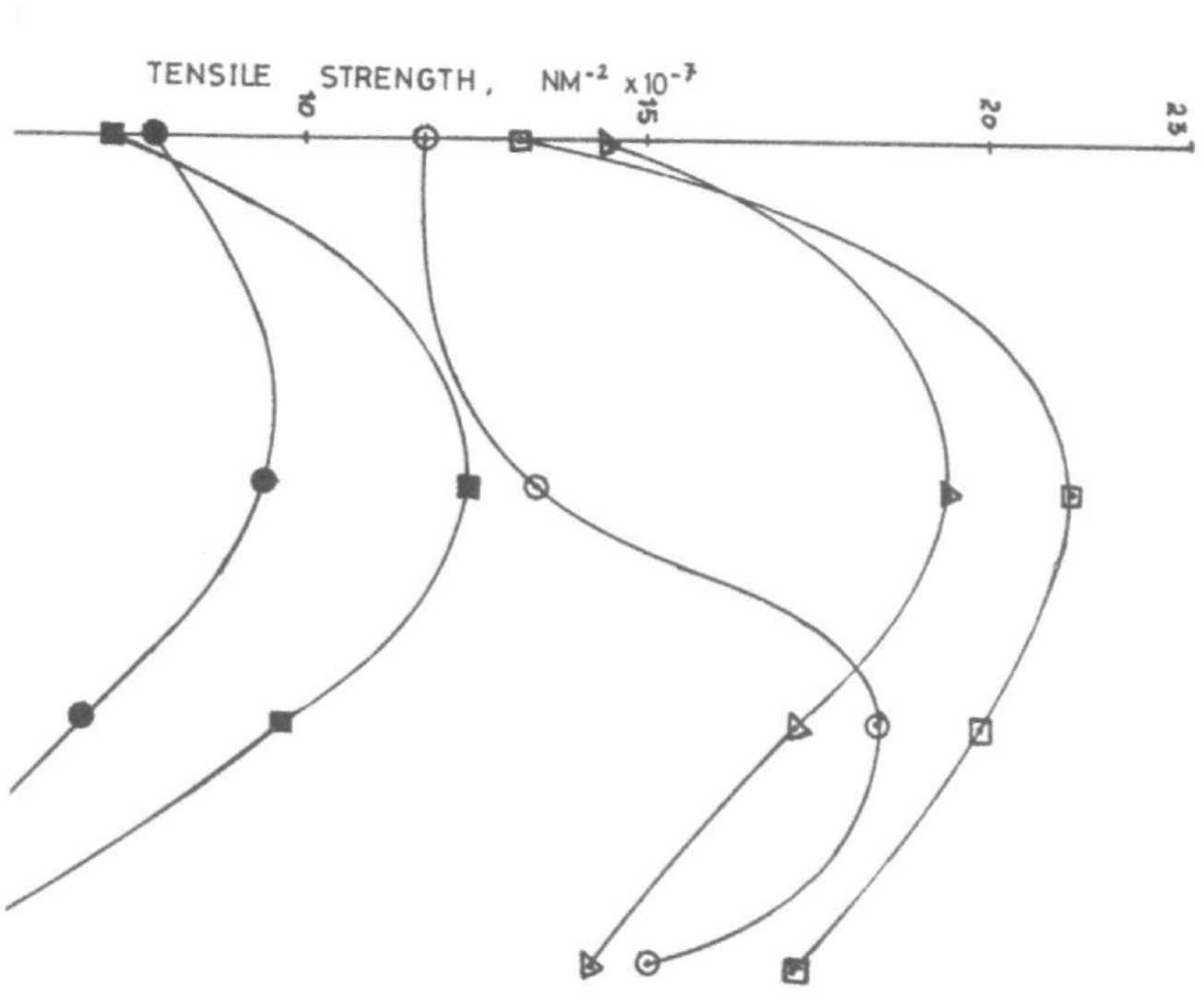
3.1.3. Effect of Plasticization on the T.S. of PVAc films

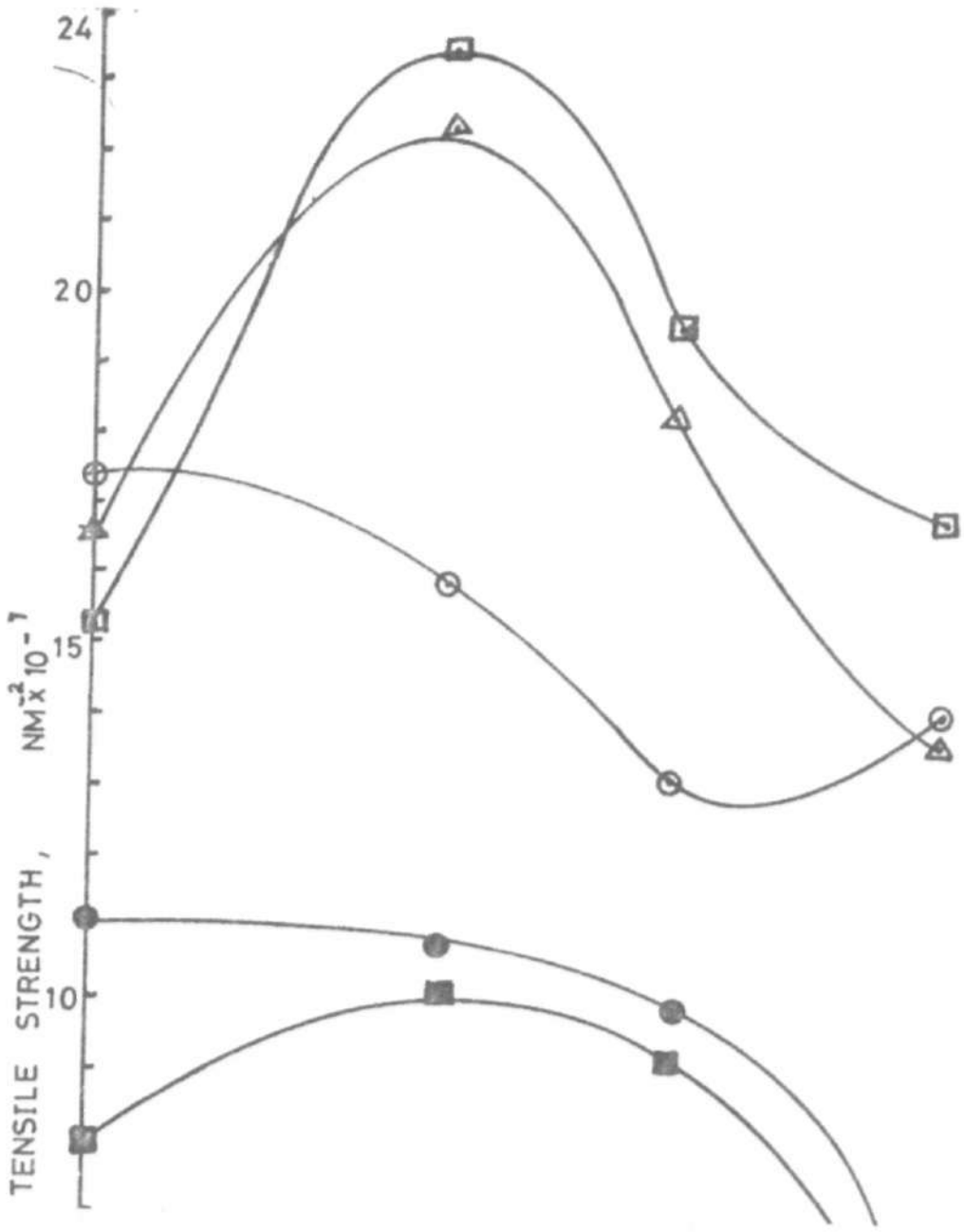
The general influence of plasticisation on the tensile strength of the cast films are shown in figures (3-1), (3-2), (3-3) also Plasticisers are non-volatile solvents with molecular weight of at least 300. Because of their size, they dissolve into the polymer and are not easily removed. The influence of solvent on the tensile strength of plasticised polymer films is difficult to assess. This is because of the possibility of interaction between the solvent used for casting films and the plasticiser. It is generally conceived that there should be some influence of the solvent on the plasticiser action.

A significant decrease in tensile strength of films used is as a result of the reduction of polymer-polymer contacts by the plasticiser. The greater the interaction, the more the spacing effect between polymer-polymer will be offset.[4,5]

The polymer films were plasticised to the extent of 10% of total polymer-plasticiser weight. The results in fig (3-1, 3-2, and 3-3), indicate a significant decrease in T.S. Again T.S. increases to a maximum and then decreases. For the two solvents, acetone/methanol and chloroform systems, films cast for the polymer products of 5 hours polymerisations show an initial increase in T.S. which reaches a maximum value with increase in % DVB content in monomer mixtures. There is then a decrease in T.S. for films of higher degrees of % DVB in bath. Maximum T.S. value for films cast from acetone/methanol is obtained at about 0.17% DVB while for those cast from chloroform, the maximum is for 0.13% cross-linking agent content. Again films from acetone/methanol have higher T.S. values than those from chloroform. Films from benzene became too sticky on plasticisation and could not be used for testing.

The tests performed on plasticised polymers which were produced at 8 hours are reported in fig 3-2. For these products, films cast from chloroform have higher value of T.S. than those cast from acetone/methanol. This is at variance with the results observed and discussed for the unplasticised materials.


TENSILE STRENGTH, NM^{-2} x10^{-7}
10
15
20
25


24
20
15
10
TENSILE STRENGTH, NM^{-2} x 10^{-7}

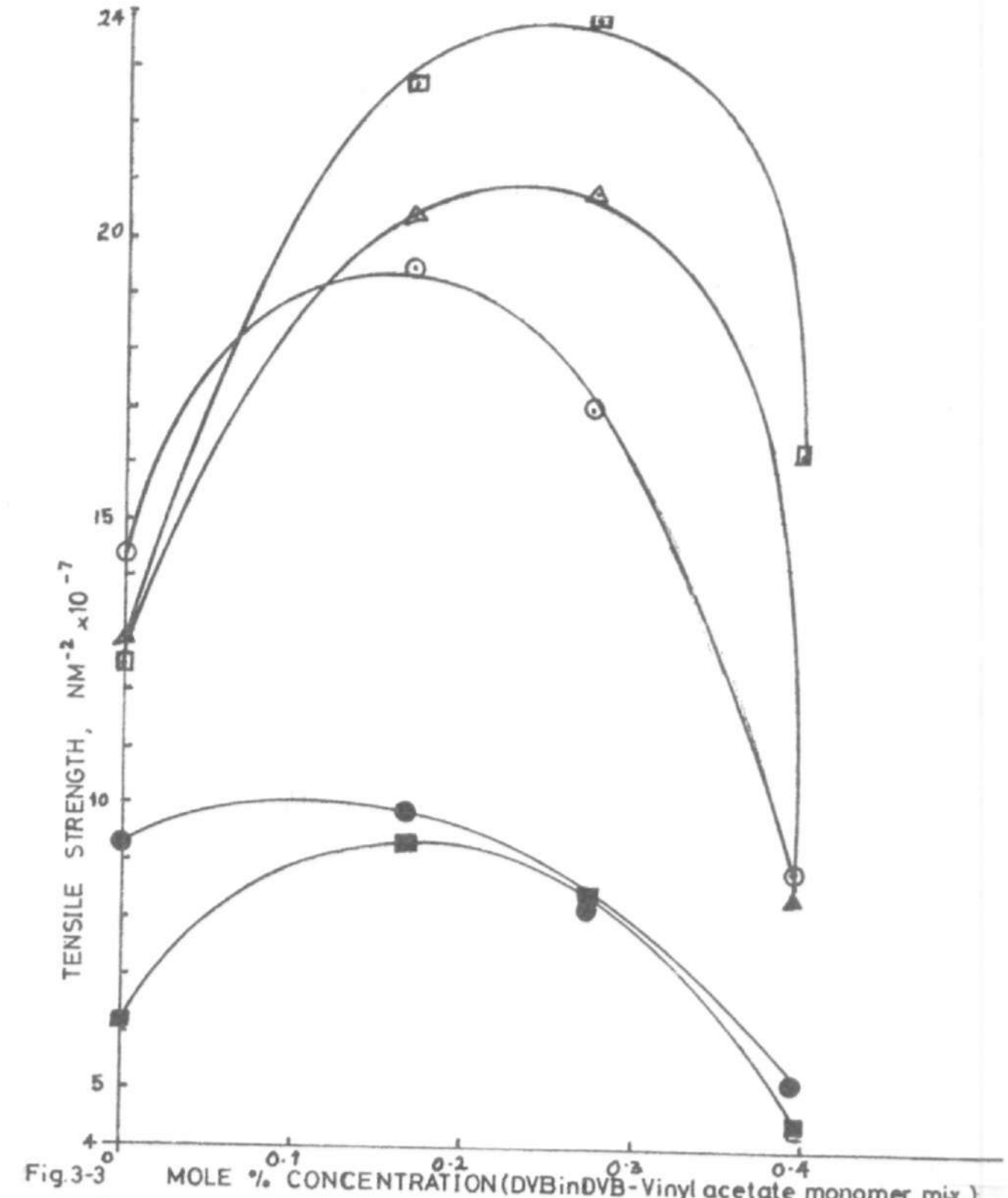


Fig.3-3 Effect of Cross-linking on the tensile strengths of films cast from different solvents using Eleven hour polymerisation products.

Unplasticised: ○ Chloroform □ Acetone/Methanol △ Benzene
Plasticised: ● Chloroform ■ Acetone/Methanol
(Films plasticised and cast from benzene were too tacky and hence unsuitable for testing)

Our earlier assumptions might however be correct, that there might be some sort of interactions, cooperative or otherwise, between the plasticiser and solvent. Again films from benzene on plasticisation became too sticky and could not be tested.

The results in fig 3-3 for plasticised samples also suggest that plasticisation of PVAc during film casting from acetone/methanol mixture may be more effective than in the presence of chloroform. Here again the tensile strength values for films cast from chloroform are higher than those from acetone/methanol mixture. The increase to a maximum of T.S. with % DVB in monomer mixture is observed. Also there are no results for the films cast from benzene on plasticisation for reason already given.

For all the plasticisation studies, a conclusion is drawn that plasticisation decreases tensile strength of poly(vinyl acetate) as is previously known,[6] including the cross-linked samples. The extent of lowering of the tensile strength has been found to depend on both the solvent used for casting the film and the amount of cross-linking agent in the polymer used as sample. Benzene appears to have a cooperative plasticisation activity with dibutyl phthalate when present with the latter and used to cast films of PVAc. It might be necessary to study the interaction of benzene with DBP.

3.1.4.

Dependence of Elongation on the extent of Cross-linking in PVAc.[7]

Fig. 3-4 shows the values for elongation at break in respect of films of PVAc. The films are from the 5 hours polymerisation products of different extent of cross-linking i.e. % DVB in reaction mixture, and were cast from different solvents.

The films cast from chloroform show a peak value of 240% elongation for the unplasticised polymer (corresponding to 0.17% cross-linking agent) after an initial rise from about 112%. It decreases thereafter with increase in the percentage of cross-linking agent in the polymerisation bath. For films cast from acetone/methanol, elongation does not seem to vary conspicuously with the amount of cross-linking agent in the polymerisation bath for the 5 hour polymerisation. It appears to have a constant low average value of about 20%. The results observed for films cast from benzene are similar to those from chloroform, with a maximum elongation of about 224%. For the plasticised samples, there is an increase in % elongation for all the films cast from chloroform and a slight increase for all cast from chloroform and a slight increase for all cast from acetone/methanol. Films from benzene on plasticisation became unusable for the mechanical tests. It has been observed that films cast from acetone/methanol mixtures have very low elongation.

Fig. 3-5 shows the elongation-at-break for the 8 hour polymerisation samples, from cross-linked and uncross-linked polymer products. The films cast from benzene show the peak value of elongation of 293% in the presence of large amounts of DVB. There was first a small decrease in elongation, followed by the rise to the peak. Films cast from acetone/methanol show very low values of elongation for most concentration of DVB, excent above 0.3% DVB in monomer mixtures, when there is a rise to about 70% elongation at about 0.39% DVB, followed by a decrease.

Again the plasticised samples exhibit increases in elongations, as would be expected. The increase in elongation of films cast from acetone/methanol is however as insignificant as the original value of elongation of the unplasticised sample. Plasticised films with benzene as solvent could not be used.

Fig 3-6 represents the elongation values for films of the 11 hour polymerisation products. The films cast from benzene show some very interesting elongation pattern, as observed for the products of 8 hour polymerisations. The peak value of 384% is obtained from the products containing 0.28% cross-linking agent. This value drops very rapidly to a very low value in 0.39% cross-linking agent, with an elongation-at-break value of 210%.

Again there is an initial decrease in elongation from 140% before the steep rise to a maximum of 384% from chloroform, the peak value of 160% is from 0.28% cross-linking agent content. The elongation in absence of cross-linking agent is 80% while for 0.4% cross-linking agent is 86%. As for films cast from acetone/methanol, the elongations-at-break values are very low usually less than 60%. The maximum value of 50% is obtained in 0.39% cross-linking agent. There is a minimum value of about 4% elongation in 0.26% cross-linking agent.

The plasticised films have higher elongation values as one would expect, for those cast in chloroform and those from acetone/methanol. Once more the films cast from benzene in the presence of DBP could not be used for testing.

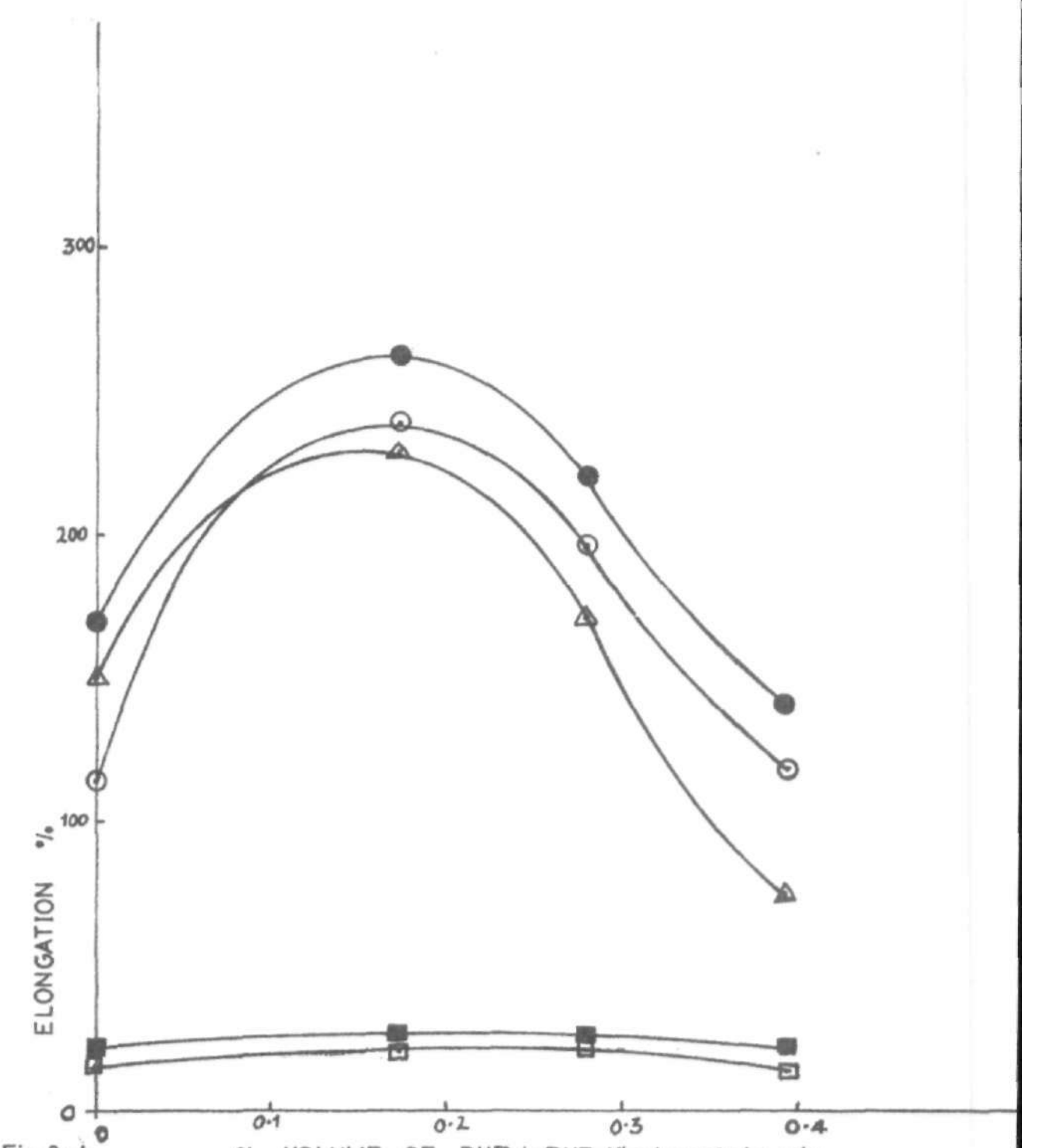


Fig.3-4

Effect of Cross-linking on the Elongation-at-break of Films of poly(vinyl acetate) using Five hour polymerisation products.

Unplasticised: ○ Chloroform □ Acetone/Methanol △ Benzene
Plasticised: ● Chloroform ■ Acetone/Methanol

(Films plasticised and cast from benzene were too tacky and hence unsuitable for testing)

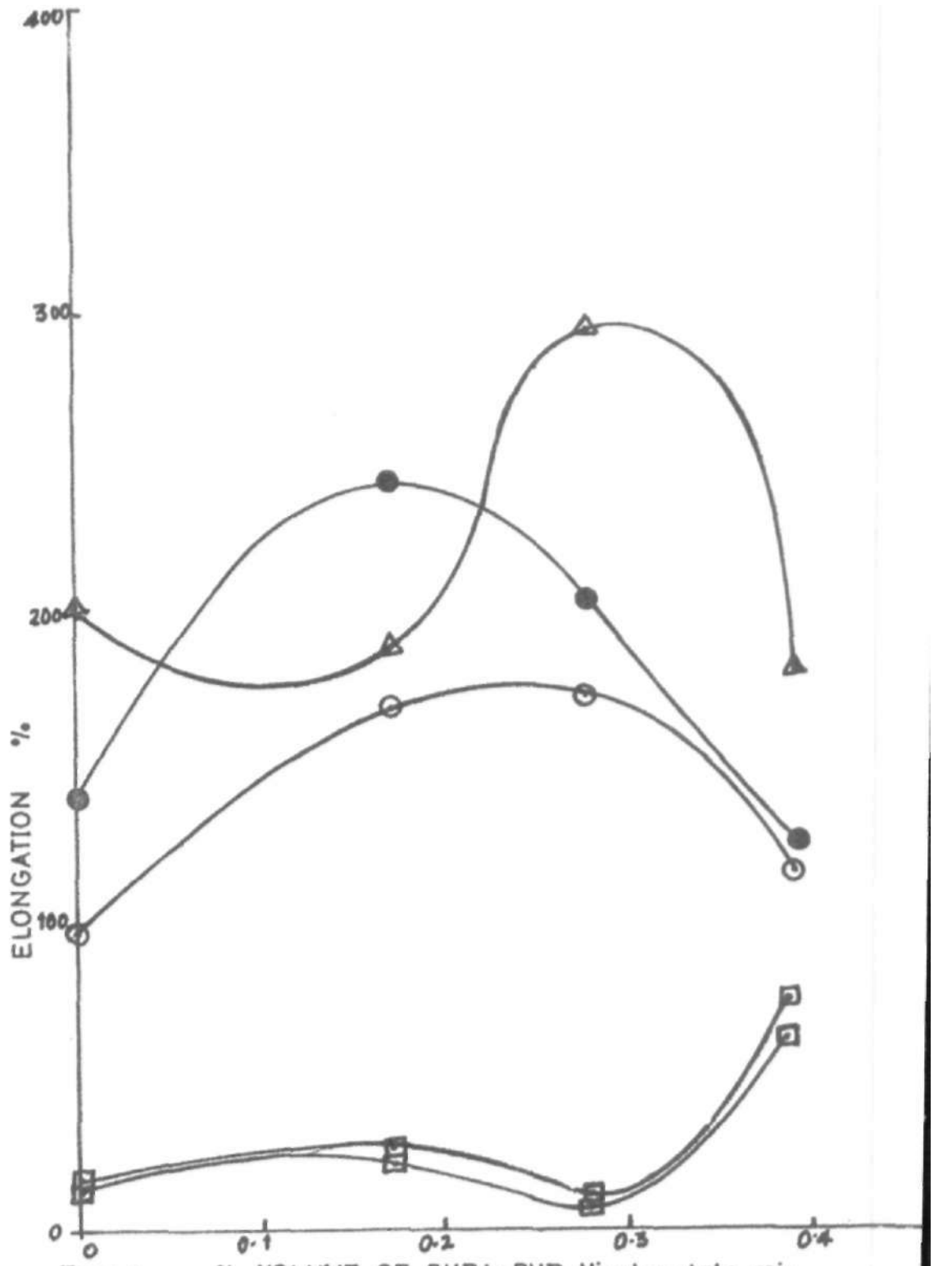


Fig3-5

Effect of Cross-linking on the Elongation-at-break of Films of poly(vinyl acetate) using Eight hour polymerisation products.

Unplasticised: ⊙ Chloroform ⊡ Acetone/Methanol △ Benzene
Plasticised: ● Chloroform ■ Acetone/Methanol
(Films plasticised and cast from benzene were too tacky and hence unsuitable for testing)

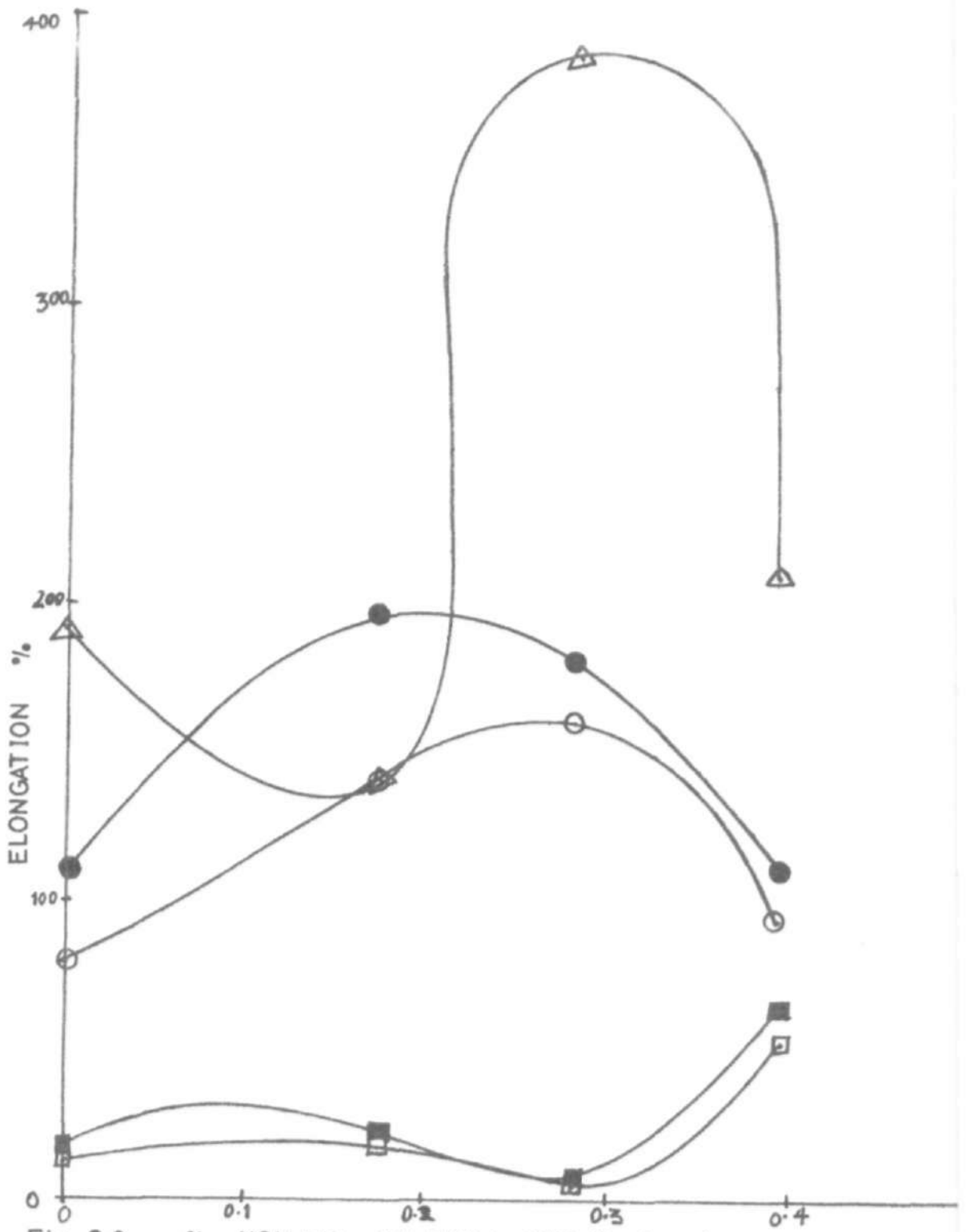


Fig. 3-6 % VOLUME OF DVB in DVB-Vinyl acetate mix.

Effect of Cross-linking on the Elongation-at-break of Films of poly(vinyl acetate) using Eleven hour polymerisation products.
Unplasticised: ○ Chloroform □ Acetone/Methanol △ Benzene
Plasticised: ● Chloroform ■ Acetone/Methanol
(Films plasticised and cast from benzene were too tacky and hence unsuitable for testing)

3.2. Bonding of metals substrates with PVAc adhesives (with or without cross-linking): Effect of heat treatment on tack.

The different samples of PVAc adhesives were prepared with acetone/methanol mixtures as solvent. The results of experiments on T.S. of PVAc films cast from three different solvents have shown the acetone/methanol mixture as being the best, of the three solvents on the account of the magnitude of tensile strength of the films. Also, the elongation-at-break of films cast from acetone/methanol mixture have been found to be the lowest. Such films have low creep hence prevent slippage of one substrate over the other on the adhesive film.[8,9,10] The adhesives thus prepared were applied on aluminium and titanium. Samples of the adhints exposed to heat for different lengths of time after which their bond strengths (tack) were measured.

Fig. 3-7 shows the variation of tack of aluminium and titanium substrates with time of heat treatment. No DVB was used during the polymerisation of the PVAc samples, and the samples tested were polymerised for 5, 8 and 11 hours respectively. Heat-treatment was at 100°C. The adhesives from the products of 5 hours and 8 hours polymerisation on aluminium substrates, show a gradual increase in tack with the increase in time of heat-treatment.

A peak value of tack is obtained with the 5 hours and 8 hours polymerisation products after 5.5 hours of heat-treatment. With the 11 hours polymerisation product adhesives the peak value is obtained at 5 hours heat-treatment time. Also in this case, a rapid decrease in tack with further exposure results. Initially tack of aluminium bond with PVAc is more sensitive to heat-treatment with PVAc polymerised for 11 hours, than those for 5 and 8 hours.

For titanium, the longer the exposure time, the bigger the tack. This is true for the three sets of PVAc; 5 hour, 8hr, and 11hr polymerisation products. For adhesives prepared from 5 hours and 11 hours polymerisation products, tack is maximum at about 5.5 hrs of heat-treatment while for those at 8 hrs, the peak tack value is obtained at 5hrs heat treatment.

Effect of the presence of cross-linking in PVAc is reflected in the results of tack versus time of heat treatment presented as fig. 3-8. Polymerisation of vinyl acetate was carried out in the presence of 0.17% DVB in the polymerisation mixture and the products isolated at different times were tested as adhesives. For aluminium as substrates tack increases with time of heat treatment until a maximum value is obtained at about 5.5hrs of heat treatment for samples polymerised for 5hrs. For those polymerised at 8hrs, tack reaches a maximum at 5.2hrs heat treatment, while for 11hrs preparations, tack has a maximum value

at 4.6hrs of heat treatment. The 11hrs polymerisation product adhesives show larger tack values with aluminium, than either the 5hrs or 8hrs polymerisation products for treatments lasting less than 5hrs.

Applying the same sets of adhesives on Titanium substrates, the 5hrs polymerisation adhesives show a gradual increase in tack as the heat-treatment time is prolonged. The peak value is obtained at 5.5hrs heat -treatment after which the tack value decreases slightly. For the 8hrs polymerisation adhesives a rapid increase in tack value with period of exposure is obtained until the maximum is reached at 5hrs of heat-treatment. A slight decrease in bond-strength is observed with 11hrs polymer product adhesives, a rapid increase in tack to a peak at 4.5hrs of heat-treatment is observed. This is followed by a gradual decrease.

Using the polymer products cross-linked with 0.28% (DVB in DVB-vinyl acetate monomer mixtures), fig. 3-9, shows that, with aluminium as substrates, and using the 5hrs polymerisation adhesives, the lowest tack value is obtained from the 3hrs of exposure to heat and increases steadily to a peak value at about 4.8hrs heat-treatment. A gradual decrease follows. With 8hrs polymerisation adhesives, the tack increases from its lowest value at 3hrs heat-treatment to a peak value at 4.25hrs of heating and later decreases to a minimum value at 5.5hrs of heat-treatment.

TABLE 3-2.1.

Polymer: time of Polymerisation.	Amount of cross-linking agent. % wt in mixture	Peak tack value Aluminium substrates kg cm^{-2}	Time of heat treatment for peak tack value HRS	Peak tack value Titanium substrates kg cm^{-2}	Time of treatme peak ta HR
5hrs.	0	32.5	5.5	53.4	5.5
8hrs.	0	44.5	5.5	63.5	5.2
11hrs.	0	44.0	5.0	61.5	5.5
5hrs.	0.17	40.5	5.5	50.8	5.5
8hrs.	0.17	44.0	5.2	53.5	5.0
11hrs.	0.17	43.5	4.7	54.5	4.5
5hrs.	0.28	26.7	4.7	41.1	4.7
8hrs.	0.28	29.0	4.3	34.5	4.5
11hrs.	0.28	37.5	4.8	43.8	4.0

The 11hrs products give high bond strength. The lowest value is obtained at 3hrs of heat-treatment, and increases as the period of heat-treatment increases. The peak is attained at 4.5hrs of heat-treatment. A decrease follows at longer periods of heat-treatment.

With the adhesives applied on Titanium, the 5hr polymer products show an increase in tack with increase in heat-treatment time, reaching a maximum at 4.5hrs heat-treatment. A steady decrease in tack value follows at longer times of heat-treatment. With the 8hrs polymerisation adhesives, the tack values are lower than for the corresponding test samples for the 5hrs polymerisation products. The peak tack value occurs at 4.5hrs heat-treatment after which a rapid decrease in tack follows.

Using the 11hr polymerisation products on titanium, the peak value is obtained at 4hrs of heat-treatment. This is followed by a fast decrease in tack value at longer times of heat-treatment.

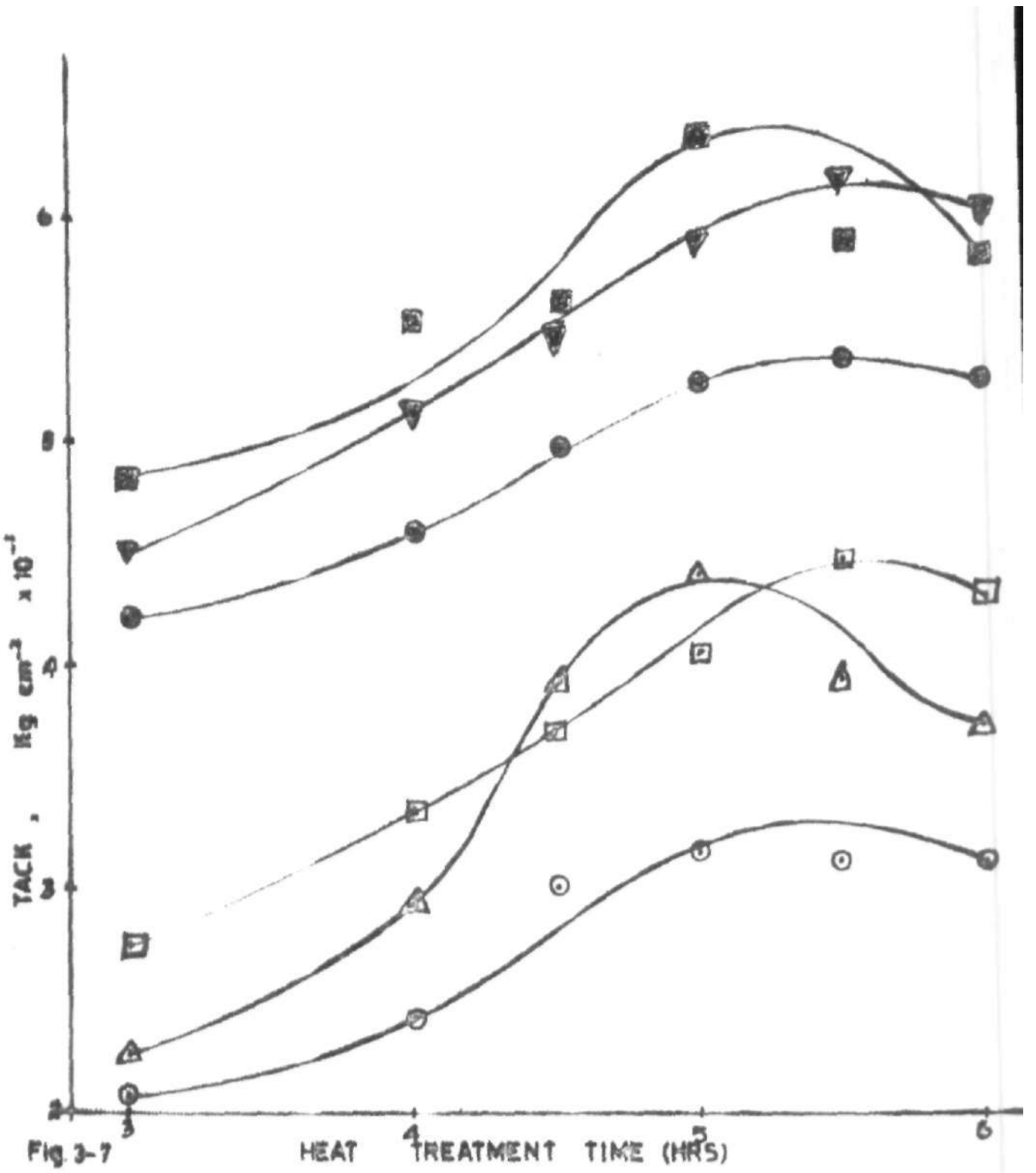


Fig 3-7

Effect of heat-treatment (periods) on tack.
No Cross-linking in the adhesives used on substrates.

Aluminium as substrates
○ 5hrs □ 8hrs △ 11hrs

Titanium as substrates.
● 5hrs ■ 8hrs ▼ 11hrs

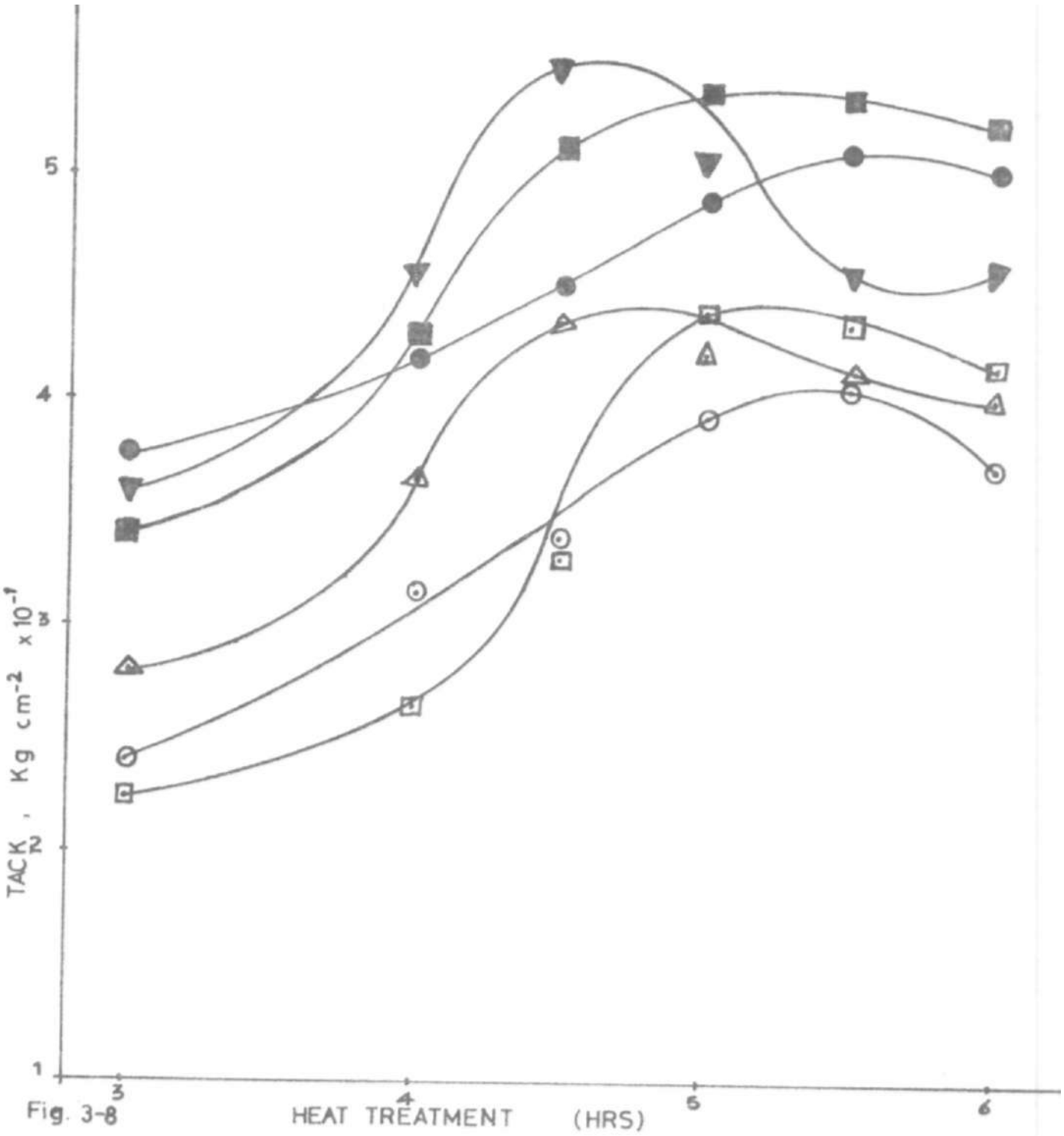


Fig. 3-8

Effect of heat-treatment (periods) on tack.
0.17% (DVB in DVB-vinyl acetate monomer mixture) used for Cross-linking.

Aluminium as substrates
○ 5hrs ⊡ 8hrs Δ 11hrs

Titanium as substrates.
● 5hrs ■ 8hrs ▼ 11hrs

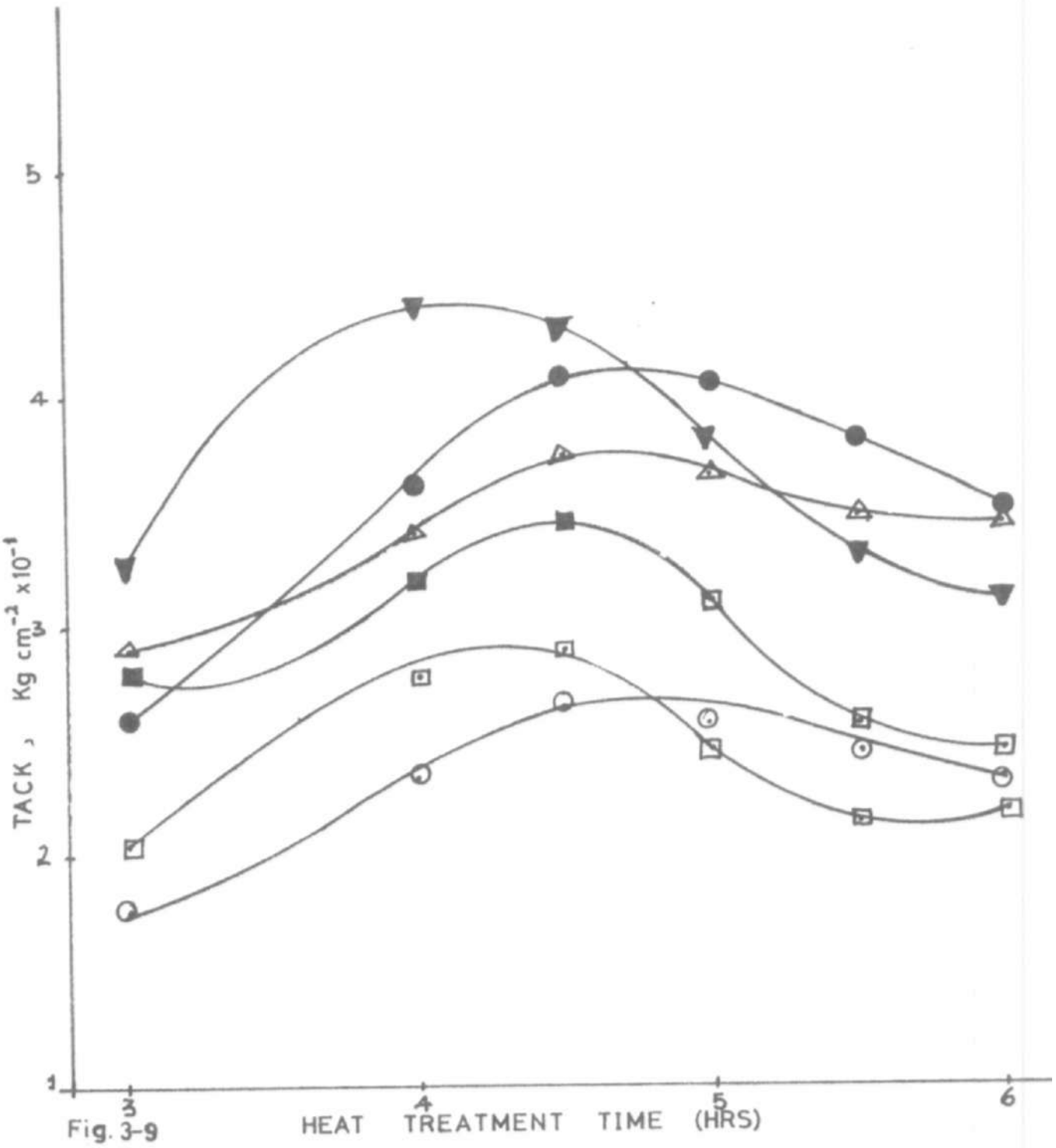


Fig. 3-9

Effect of heat-treatment (periods) on tack.
0.28% (DVB in DVB-vinyl acetate monomer mixture) used for Cross-linking.

Aluminium as substrates
○ 5hrs ⊡ 8hrs △ 11hrs

Titanium as substrates.
● 5hrs ■ 8hrs ▼ 11hrs

3.2.1. COMPARISON OF RESULTS FOR THE TWO SUBSTRATES.

Table 3-2.1, shows the peak values for the tack of aluminium and titanium substrates. The polymers used (in terms of hours of polymerisation and amount of DVB present in the mixture) and the time of heat treatment are shown. The tack values in respect of titanium substrates are high compared to those for aluminium using the same adhesives the surfaces of the two adhints having been treated as recommended.[11] The high bond strength exhibited by titanium is expected, because the metal does not oxidize when exposed to the atmosphere. With some other metals e.g. aluminium, Zinc, their surfaces are coated by their oxides which are formed on exposure to the atmosphere, even after the best surface treatment. These oxides are impurities that may result in microscopic points of nonbonding, uniformly distributed over the adhesive - substrate interface. These nonbonding points will not only affect the strength of the overall bond but also affect the wave coupling between the substrate and the adhesive.[12]

Considering the uncross-linked polymer adhesives, the 8hrs polymerisation product gives the best tack in both aluminium and titanium substrates, at heat-treatment time of between 5 and 5.5hrs.

The polymer adhesives containing 0.17% cross-linking agent in polymer mixture, show that 8hrs polymerisation product is once again best suited to aluminium while the 11hrs product gives the largest tack value with titanium.

It is again shown that the 11hrs polymerisation polymer product gives the highest tack value in both aluminium and titanium when polymers containing 0.28% cross-linking agent in polymer mixtures are used.

From the tack values in table 3.2.1, it is seen that 8hrs and 11hrs uncross-linked polymer products and all samples in the 0.17% cross-linking agent content in polymer products give aluminium reasonably high tack values. However, when the cross-linking agent contents goes beyond 0.17%, tack values fall. With titanium substrates however, the more the cross-linking agent content in polymer, the less the tack values. This uncooperative association between adhesives and adhints in the case of titanium, may be due to the fact that the pores on the surfaces of titanium are not large enough to adsorp the three-dimensional molecular volume of the cross-linked adhesives. The more the cross-linking agent content in polymer, the larger the molecular volume. When wetting of substrate is poor, tack is low.[13]

The results generally show that cross-linking in PVAc reduces the adhesive properties and specifically reduces the tack for bonds between aluminium or titanium.

3.3. Comparative Study: Effect of plasticisation on Tack of heated and unheated bonded substrates

The adhesives used in the comparative studies are the products of 5hrs, 8hrs, and 11hrs., Polymerisation time. They contain different amounts of cross-linking agent in their polymer make-ups. The adhints used are:- Aluminium, Zinc and Titanium. Some factors which could be said to account for differences in tack values are:- oxide formation on substrates,[12] different sizes of the pores on the surfaces of substrates, and intramolecular attractions between adhesives and adhints.[13] When a solvent is trapped in an adhesive, the latter can not develop full bond-strength when used in bonding of substrates because of the interference[5] of the molecules. Also, if the PVAc adhesive is plasticised, a decrease in tensile strength[6] is expected. As has been pointed out 3.1.3., there might be a sort of interaction "cooperative or otherwise," between the plasticiser and solvent. This might cause more of the solvent used in making the adhesive to be retained in the adhesive between the substrates and consequently lead to reduction in bond strength.

3.3.1. Heated and unheated bonded Aluminium Substrates.

Four samples of aluminium lap-joints were used for each of heated and unheated tests employing each type of the available adhesives. The tack values are represented by figures 3-10, 3-11, and 3-12.

In fig. 3-10, where 5hr. polymerisation PVAc products were used, there is a decrease in tack for unheated adhints as the quantity of cross-linking agent in polymer is increased, till a minimum value at about 0.28% cross-linking (DVB in the system) is reached, after which the tack value increases slightly. The samples heated at 100^{o}C for 3hrs show an initial increase in tack value for cross-linking agent in the system of up to 0.13%. Then a decrease in tack value is observed attaining a minimum value for about 0.30% cross-linking agent in system. Then an increase in tack value is noticed again. The plasticised adhesives show lower tack values for each of corresponding treatments of unplasticised samples.

For the 8hrs, unplasticised and plasticised polymerisation products, the same pattern is observed as for the unplasticised 5hr products, though the numerical tack values in the 8hr polymer products are higher than those of the 5hr products. The zero cross-linking tack values are the highest tack just as in the 5hr. products, and the minimum also at 0.30% cross-linking agent in polymer system, followed by a slight increase in tack.

For each of these sets of study, tack decreases through a minimum and does not show any maximum value. Tack values for the heated and unheated adhints are presented in fig. 3-12, for the plasticised and unplasticised 11hr polymerisation PVAc adhesive products. The pattern of variations in tack differs for heat-treated and unheated adhints when compared to the pattern obtained for the PVAc products of 5 and 8 hour polymerisations. The tack for the unheated adhints show initial decrease in values, reaching a minimum at about 0.15% cross-linking (DVB in the system). The tack thereafter increases attaining a peak at about 0.28% cross-linking (DVB in the system). Then the tack decreases. For the adhints which were heated, the tack gradually increases with increase in the amounts of cross-linking agent in the system. At about 0.25% cross-linking agent in the system, the tack attains a peak, and then rapidly decreases. For the adhints joined with plasticised adhesive, the same pattern as in the unplasticised adhesive joints is shown though with lower tack values.

3.3.2. Heat-treated and untreated bonded Zinc Substrates.

Zinc substrates on which plasticised and unplasticised 5hrs polymerisation PVAc adhesive products were administered, show different patterns of tack increases and decreases. Fig. 3-13. For the unheated substrates, the tack decreases from some initial values, attaining a minimum in each case, corresponding to about 0.28% (DVB in the system). This is followed by an increase.

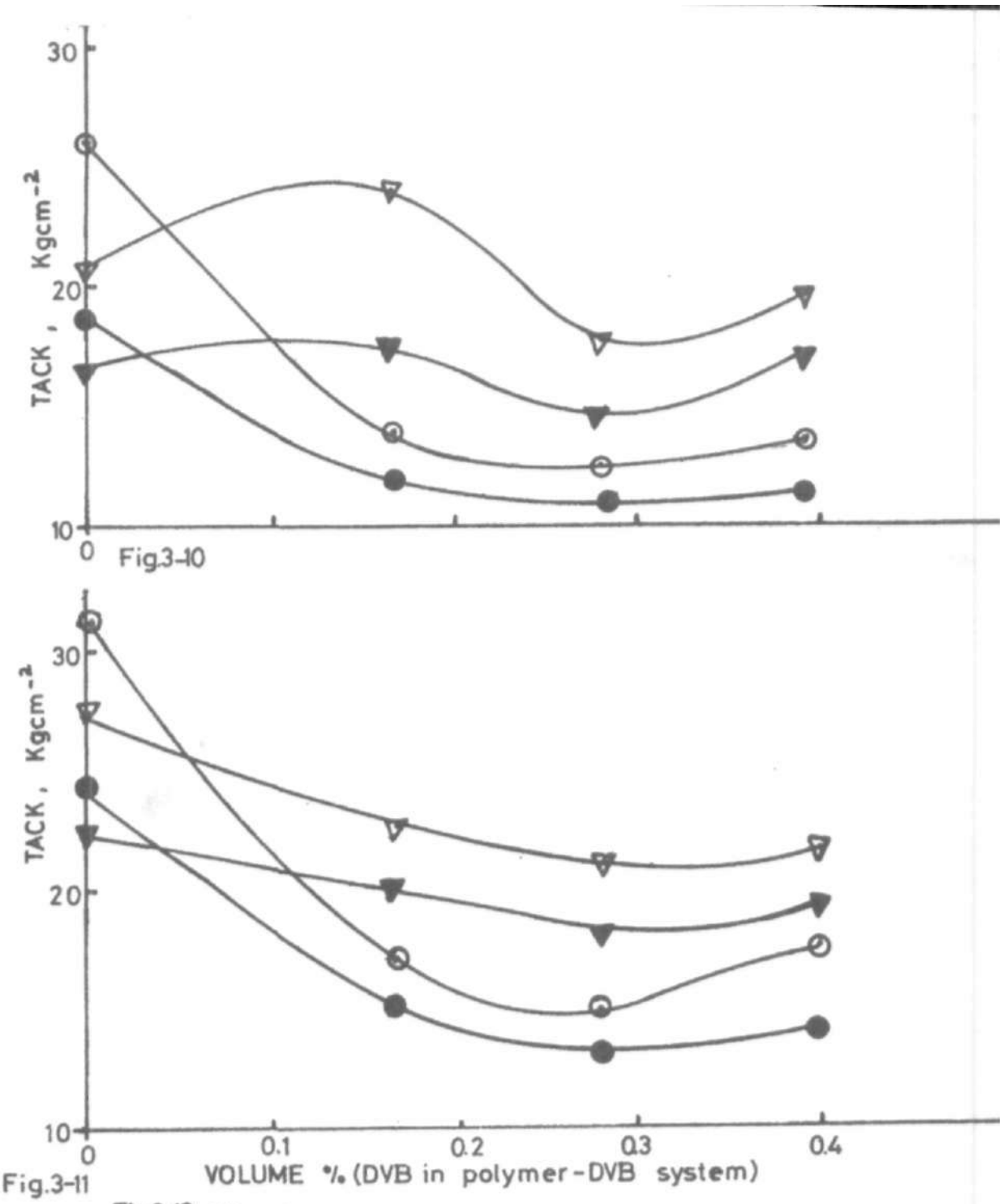


Fig3-10 Five hour polymerisation product:

Fig3-11 Eight hour polymerisation product:
Variation of Tack with the amount of DVB in the PVAc showing the effect of plasticisation on tack for unheated, and heated (3hrs) bonded substrates. (Aluminium)

○ Unplasticised unheated lap-joints
● Plasticised unheated lap-joints
▽ Unplasticised heated lap-joints
▼ Plasticised heated lap-joints

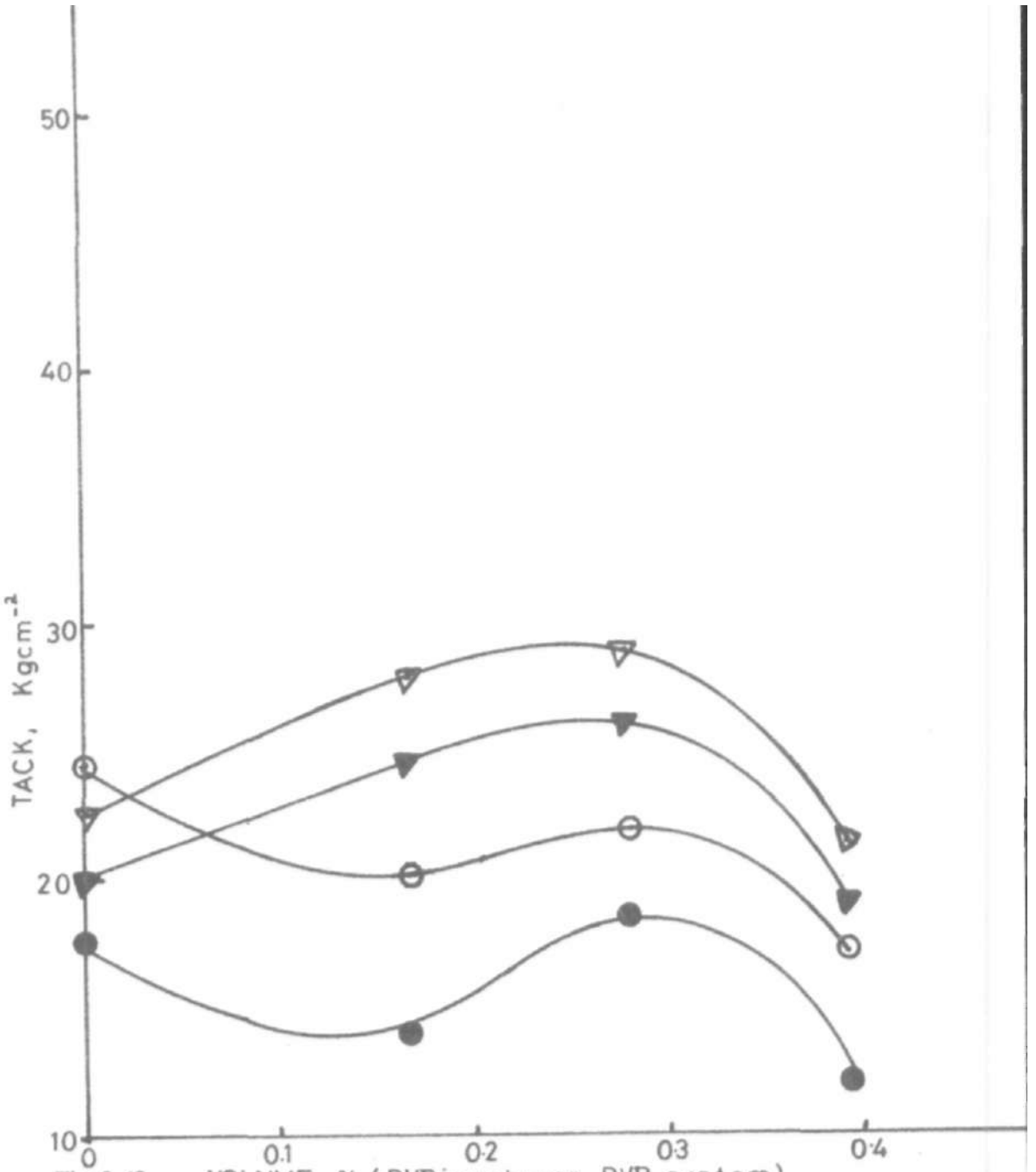


Fig.3-12 Eleven hours polymerisation products.
Variation of Tack with the amount of DVB in PVAc, showing the effect of plasticisation on tack for unheated and heated (3hrs) bonded substrates. (Aluminium)

○ Unplasticised unheated lap-joints
● Plasticised unheated lap-joints
▽ Unplasticised heated lap-joints
▼ Plasticised heated lap-joints

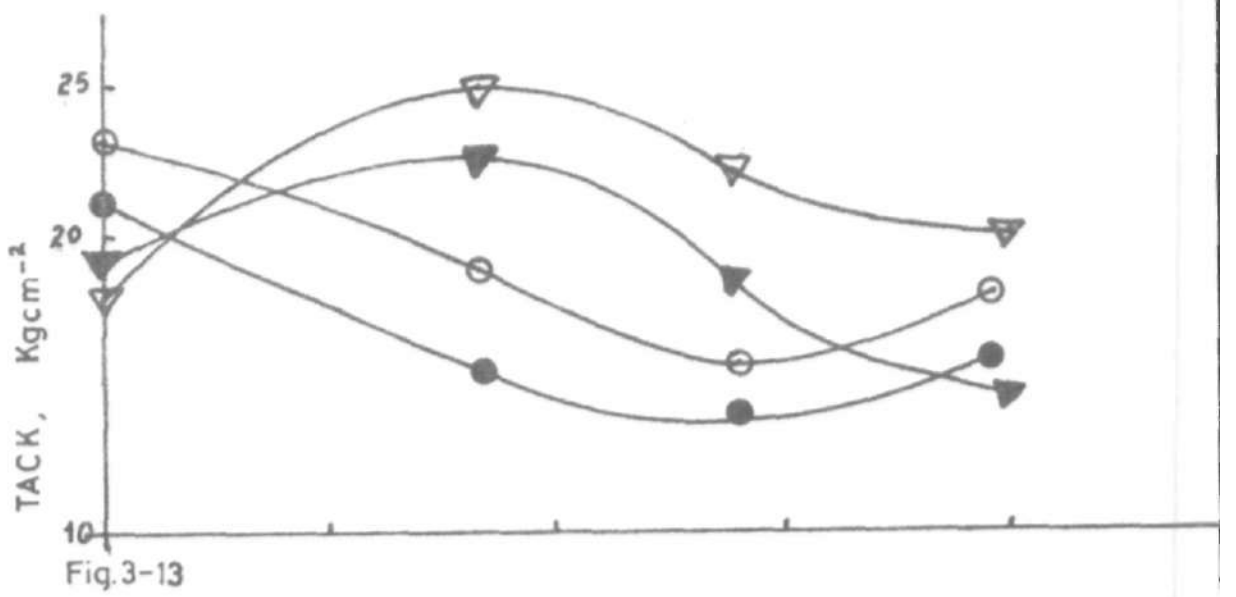


Fig.3-13

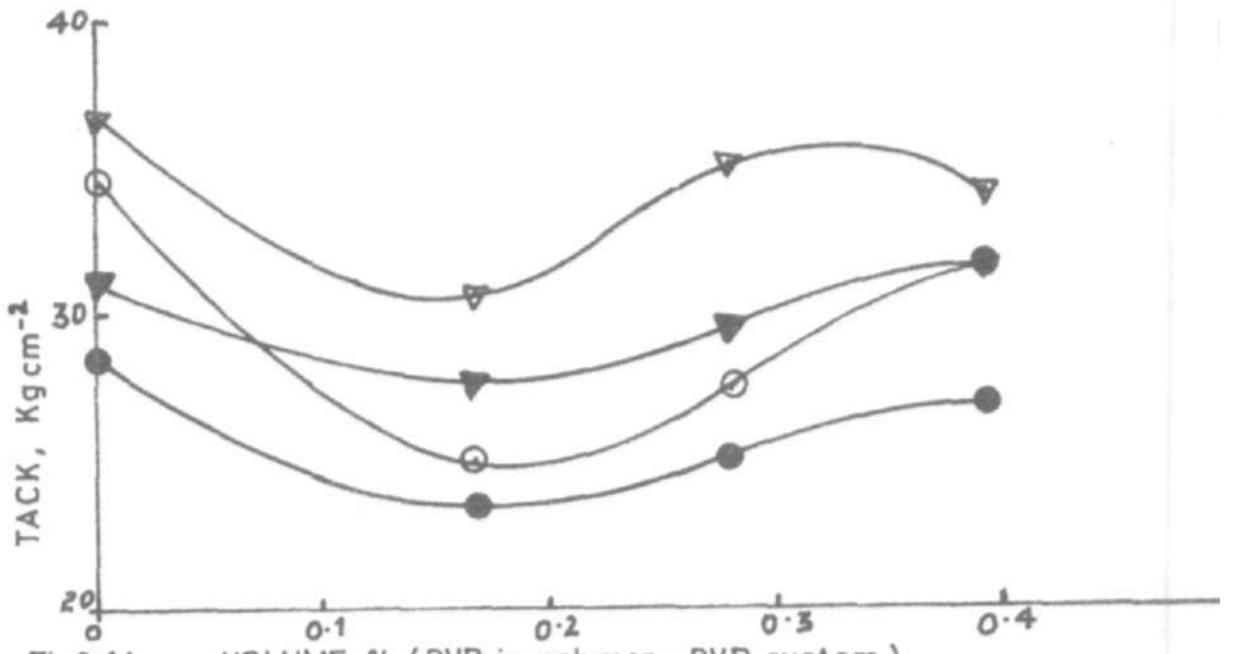


Fig.3-14 VOLUME % (DVB in polymer - DVB system)

Fig.3_13 Five hour, polymerisation products.

Fig. 3_14 Eight hour polymerisation products.

Variation of Tack with the amount of DVB in the PVAc showing the effect of plasticisation on tack for unheated and heated (3hrs) bonded substrates. (Zinc)

○ Unplasticised unheated lap-joints

● Plasticised unheated lap-joints

▽ Unplasticised heated lap-joints

▼ Plasticised heated lap-joints

For the heated samples, increase in tack values is observed initially, reaching a peak at about 0.17% cross-linking (DVB in the system), which is then followed by a decrease. When 8hr polymerisation products were used as adhesives, fig. 3-14, each set of the unheated samples again shows an initial decrease in tack going through a minimum at about 0.17% cross-linking agent, followed by an increase as the amount of the cross-linking agent increases. The heat-treated adhints also show initial decreases attaining a minimum at about 0.17% cross-linking (DVB in the system). The unplasticised adhints show an increase in tack from the minimum tack value until a second peak, lower in value than the initial tack, is attained at about 0.32% cross-linking content in polymer, followed by another decrease in tack. Also for the plasticised adhesives, tack decreases to a minimum and then increases.

The results of the study on the 11hr polymerisation PVAc adhesive products are represented in fig. 3-15. The initial bond strength is the highest in both plasticised and unplasticised unheated adhints. It then decreases with introduction and increase in amount of cross-linking agent. When heated, the bond strength of the adhints joined with unplasticised adhesives also decreased from an initial highest value to a minimum which is ill-defined and then increased, to a peak at about 0.28% cross-linking agent in system, then followed by a decrease.

The effect of plasticisation is reflected in reduction of the bond strength, though the pattern of variations of tack with amounts of cross-linking agent remains essentially as for unplasticised samples.

3.3.3. Heat-treated and untreated bonded Titanium Substrates.

Fig. 3-16 shows the tack values obtained from substrates which were bonded with 5hr polymerisation PVAc adhesive products. In each case, of the untreated samples, tack rises to a maximum value at about 0.13% DVB and then decreases rapidly at first and then gradually. The heated samples exhibit greater tack than the unheated samples and the effect of plasticisation of the adhesive can also be recognised in the reduction of tack throughout the range of concentration of cross-linking agent. (DVB).

For this range of concentration of cross-linking agent, the uncross-linked adhesive has the highest tack value for any given set of polymer preparations of same hour of polymerisation but different amounts of cross-linking agent. The results represented in fig. 3-17 for PVAc products of 8hr polymerisation products follow an interesting trend. There is, in each case, for the unheated samples, a steep rise in tack with amount of cross-linking agent present. A maximum is obtained for tack in each case corresponding to about 0.23% DVB. The heated bonded substrates exhibit stronger bond strength than those unheated, with the

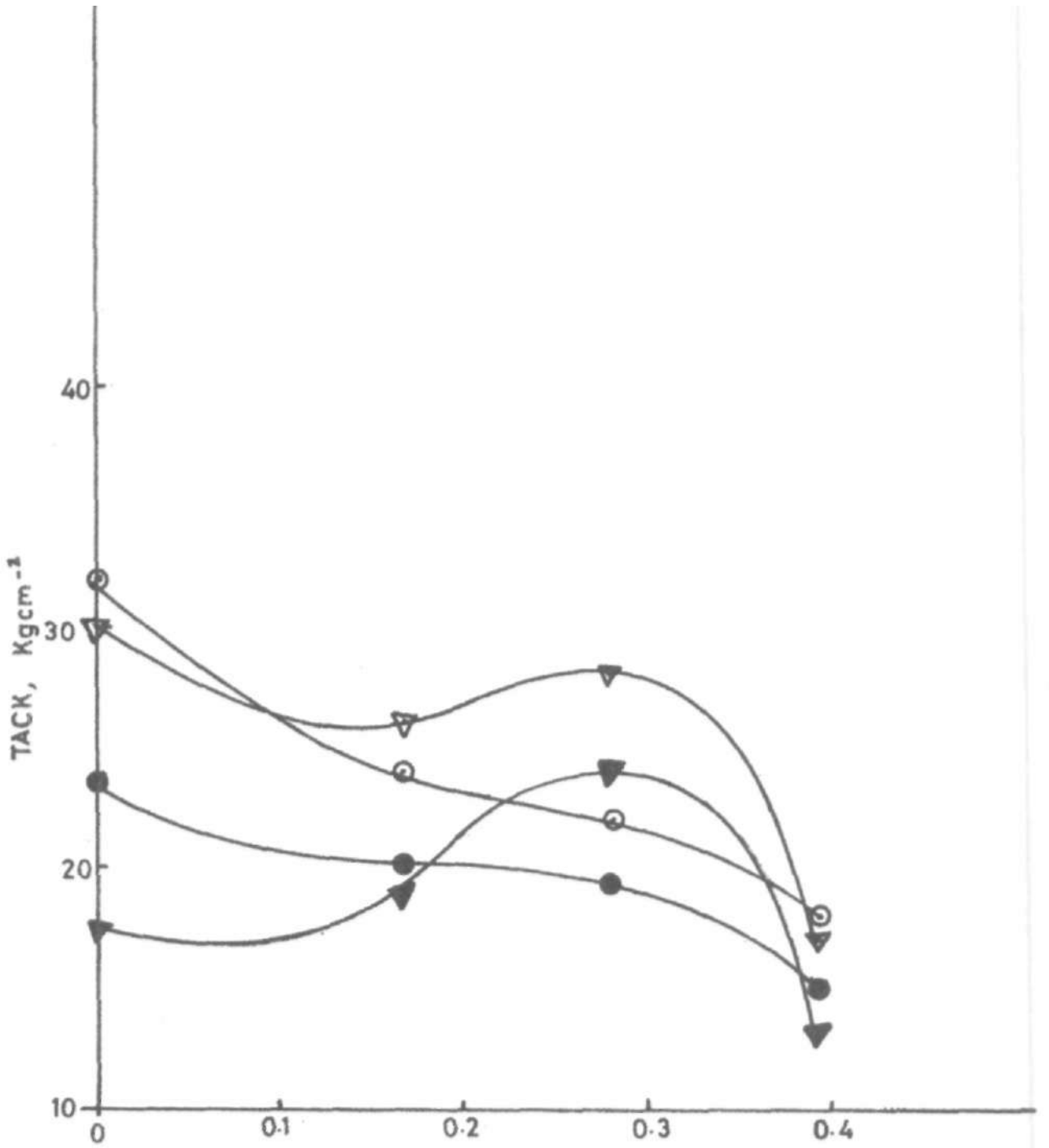


Fig.3-15 VOLUME %. (DVB in polymer - DVB system)

Eleven hours polymerisation products.
Variation of Tack with the amount of DVB in PVAc, showing the effect of plasticisation on tack for unheated and heated (3hrs) bonded substrates (Zinc)

⊙ **Unplasticised unheated lap-joints**
● **Plasticised unheated lap-joints**
▽ **Unplasticised heated lap-joints**
▼ **Plasticised heated lap-joints.**

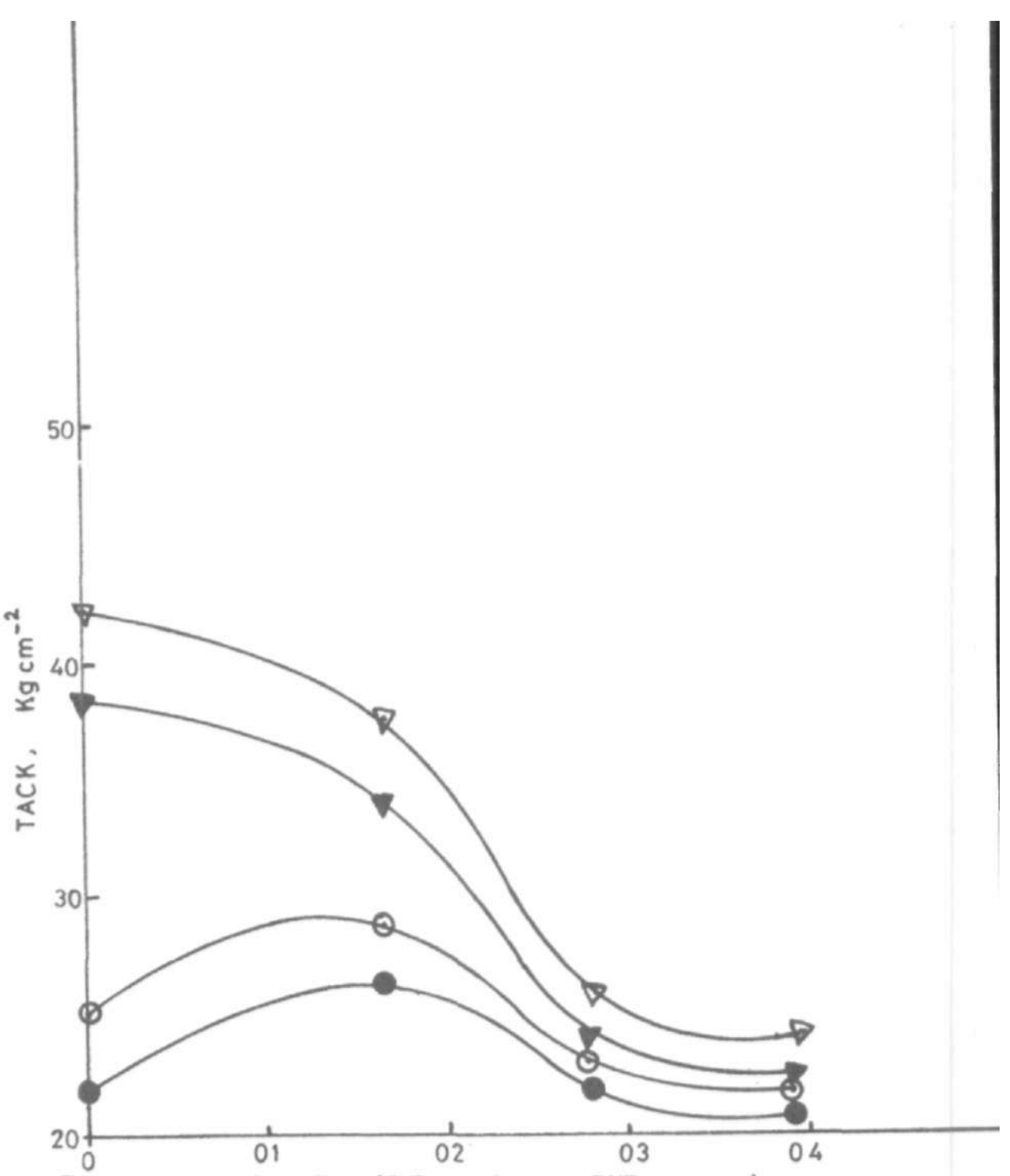
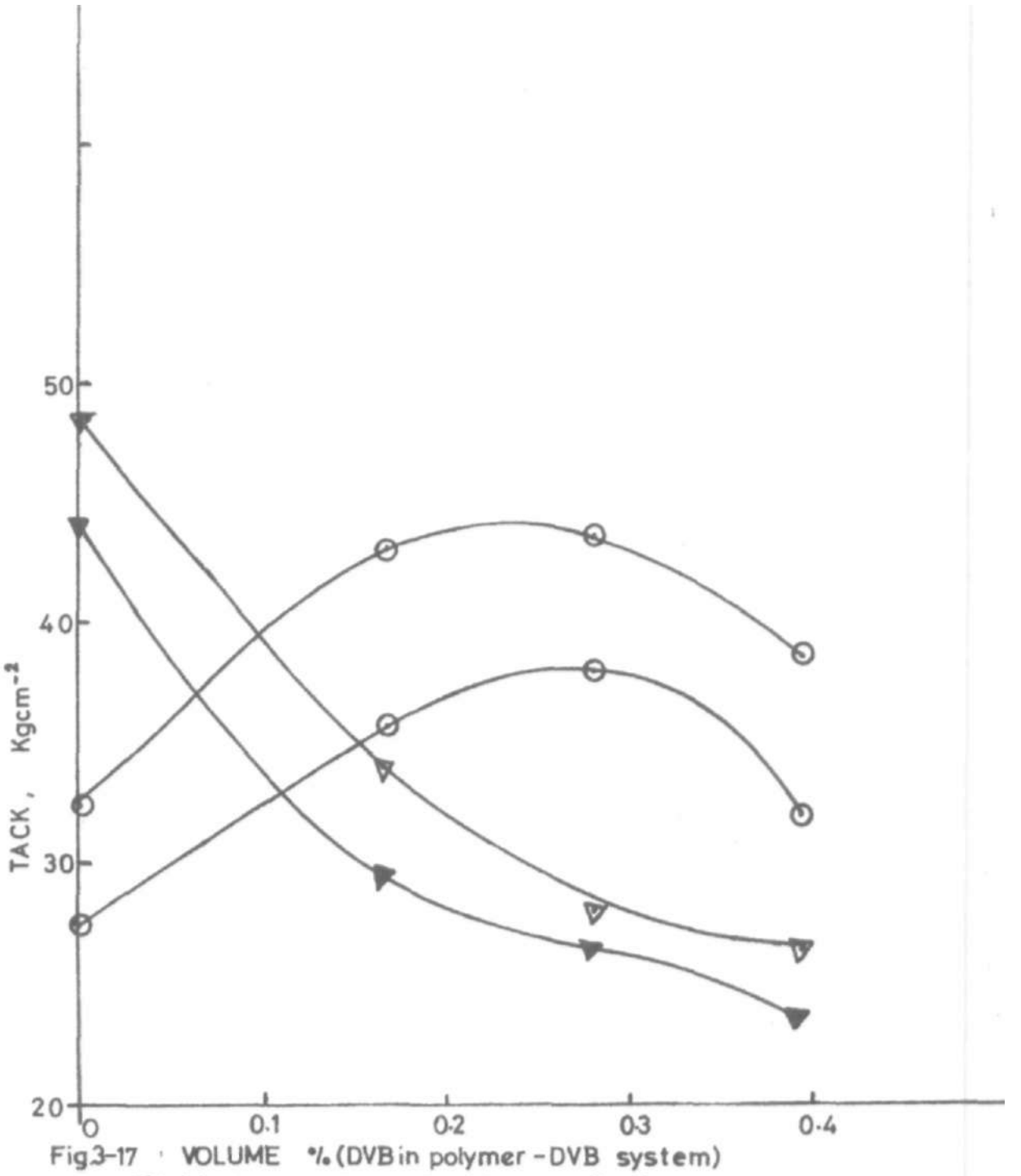


Fig. 3-16 VOLUME %(DVB in polymer - DVB system)
Five hour polymerisation products
Variation of Tack with with the amount of DVB in the PVAc, showing the effect of plasticisation on tack for unheated, and heated (3hrs) bonded substrates (Titanium)

⊙ Unplasticised, unheated lap-joints
● Plasticised unheated lap-joints
▽ Unplasticised heated lap-joints
▼ Plasticised, heated lap-joints



Eight hour polymerisation products.
Variation of Tack with the amount of DVB in the PVAc, showing the effect of plasticisation on tack for unheated, and heated (3hrs) bonded substrates (Titanium)

⊙ Unplasticised, unheated lap-joints
● Plasticised unheated lap-joints
▽ Unplasticised heated lap-joints
▼ Plasticised, heated lap-joints

polymer without cross-linking as adhesive. The tack of the heated substrates decreases very rapidly initially and more gently as the concentration of cross-linking agent (DVB) increases. Plasticisation is again observed to lead to a reduction of tack. Much higher bond strength has been recorded here for samples of 8hr polymerisations than those of 5hr polymerisations.

Fig. 3-18 shows the tack values of adhints bonded with 11hr PVAc adhesives. The pattern of tack plots for the heated and unheated substrates are very different. The unheated substrates show rapid initial increases in tack. The unheated substrates bonded with unplastricised PVAc adhesives show a peak value at about 0.28% DVB. While those bonded with plasticised PVAc adhesives have a peak for 0.17% cross-linking agent in system. The heated samples show the general decrease in bond strengths from the initial high value, as the cross-linking agent contents increase. As had been the trend in the previously observed cases, plasticisation reduces the tack both for the heat-treated and untreated samples.

3.3.4. COMPARISON OF RESULTS FOR THE THREE ADHINTS

From the results of the tack measurements of different adhints treated with PVAc of same hours of polymerisations as adhesives, the following comparison could be useful.

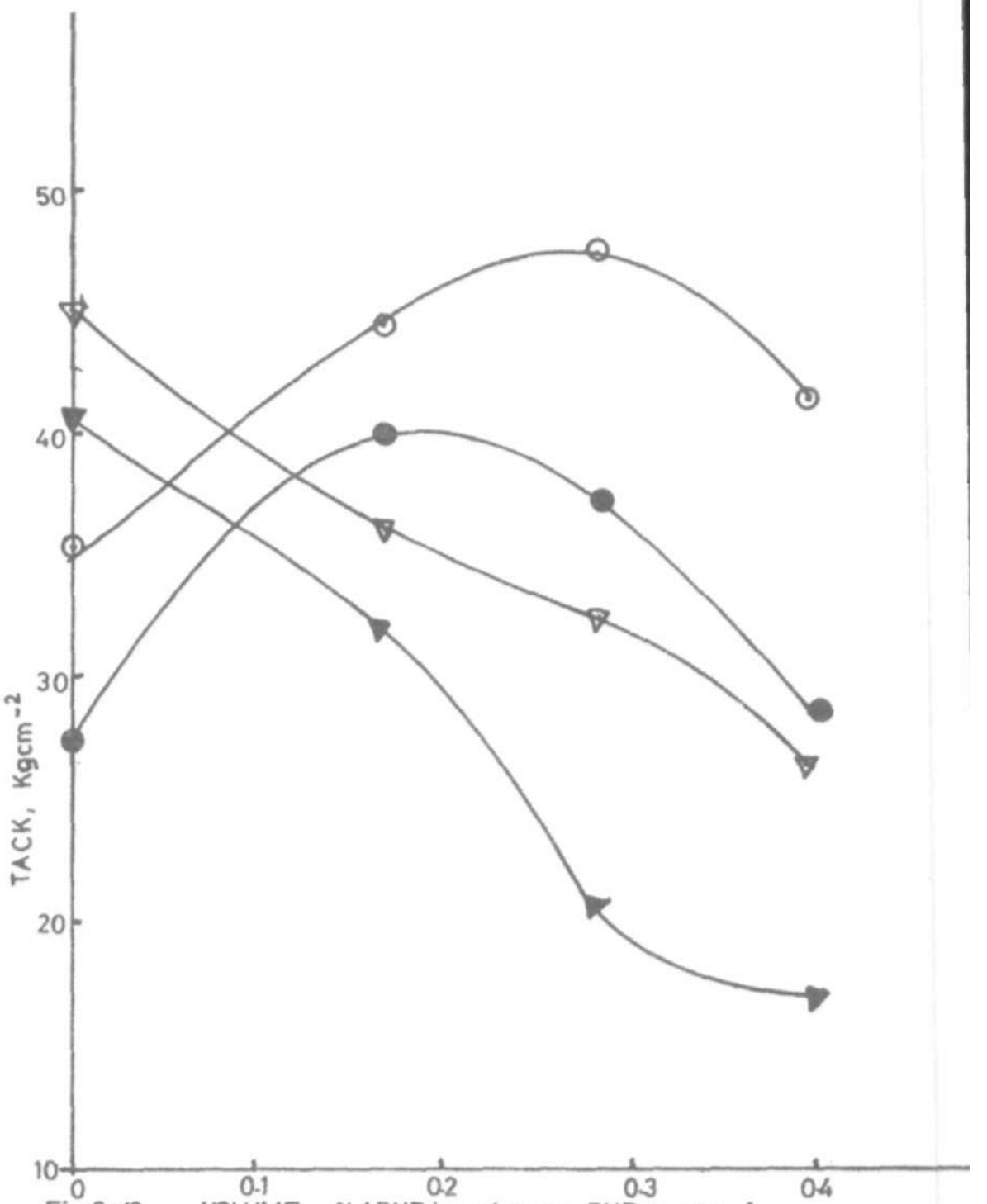


Fig.3-18 Eleven hour polymerisation products.
Variation of Tack with the amount of DVB in the PVAc, showing the effect of plasticisation on tack for unheated, and heated (3hrs) bonded substrates (Titanium)

⊙ Unplasticised, unheated lap-joints
● Plasticised unheated lap-joints
▽ Unplasticised heated lap-joints
▼ Plasticised, heated lap-joints

The 5hr polymerisation PVAc adhesive products with no cross-linking agent included in the system, show good bonding with aluminium, less for zinc, and titanium. The poor bonding in zinc could be explained in the light of the fact that zinc could easily oxidize on exposure to air. The oxides have a coating on the surfaces of the substrates and thus prevent good metal-polymer contact from being firm. Titanium is a metal with very smooth surface. Though it does not easily oxidize by mere exposure to the atmosphere, the pores on its surfaces are not much and hence there are no cavities into which the adhesives can hold onto, to properly give good bond-strength to the adhints. Also, it must be remembered that polymer products of the 5hr polymerisations would be mainly composed of straight polymer chains[15] which are capable of easy movement and this would be manifested in the poor bond strength of the substrate. The tack in each of bonded aluminium and zinc increases when heated, and with increase in cross-linking to about 0.17% cross-linking agent DVB. The tack for titanium decreases with increase in the amount of cross-linking agent.

With the PVAc adhesive of 8hr polymerisation, the tack of bonded aluminium and zinc decreased with increase in cross-linking, while an increase is observed for bonds of titanium when the bonded substrates were not heat-treated.

It would seem that heating promotes further entaglements of the cross-linked polymer chains which would then have large molecular volumes. This would prevent the pores on the titanium surfaces from being filled with enough adhesive molecules to sustain tack.[18]

Cross-linking in the elven hour PVAc adhesive polymerisation products seemed to have gone to an extent where the polymers' solubility in the solvent are greatly reduced. Most of the particles in such cases may not take part in the bonding process because the surface contact areas of sphere are very small. Therefore the aggregate contact between substrates and adhesive will be small and scattered which will result in poor tack as a result of poordiffusion.[16]

From the observations, it can be concluded that when reasonably cross-linked PVAc adhesives are to be used on titanium, it would be advisable not to heat-treat the substrates. Should heating be unavoidable, it might have to be done for about 5hrs as the previous results section 3.2.1. have suggested.

3.4. Emulsion Adhesives of PVAc.

When emulsions of poly(vinyl acetate) produced at 8 and 11hr polymerisation, were used to bond different substrates, it was observed that most of the substrates showed very low bond-strengths. This is particularly so, when the tack values so obtained from same substrates when bonded with purified adhesive

products obtained from emulsions and dissolved in acetone/methanol mixture, are compared.

In cases where the adhints were bonded, the substrates yeilded before the joints were ruptured. From the results, Table 3.4-1., it can be seen that emulsions as adhesives show high bond strengths when applied on plywood and card-board. With glass, most of the substrates themselves yeilded before the separation of adhints at points of adhesive application.

Emulsion adhesives are very poor for bonding metals. Since diffusion may not be considered as making much contribution to adhesion on the surface of highly polished metal, the poor adhesion may be explained on the basis of adsorption theory.[17] This demands that contact between the polymeric adhesive and the substrate material be close enough to facilitate interaction of molecular forces between the two bodies hence efficient wetting is of primary importance among the factors controlling adhesion and for most metal substrates, this condition is not always satisfied, hence the poor bonding. The good-bonding obtained with wood and card-board could be explained by the fact that these substrates are relatively porous and hence emulsion particles can diffuse into the pores and cause effective bonding.

Complete wetting is also desirable, and this is achieved with the cardboard and wood substrates. The polymer particles are spread over the substrate surfaces and interlocking forces increased which results in strong bonding.

From the results obtained, Table 3.4-1, it would be seen that with the 8hr emulsion, most of the high bonds were obtained when substrates were not heated. This might be due to the fact that when wood and paper are heated, the surfaces become very undulating and the cohesion forces between the substrates particles are weakened. This undulating surfaces reduce the substrate-polymer-substrate contact that should ensure good bonding. Also the greater tack from plasticised adhesive should be expected for wood and cardboard because plasticisation is expected to soften the beads of the polymer materials and this improves on spreading of adhesive over larger area of substrate surfaces.

TABLE 3.4-1.

Substrates	Unplasticised Emulsions No Crosslinking		Plasticised Emulsions No Cross-linking		Unplasticised Emulsions 0.17% DVB in system.		Plasticised Emulsions 0.17% DVB in system.		Unplasticised Emulsion 0.28% DVB in system.		Plasticised Emulsion 0.28% DVB in system.		
	TACK, Kg cm^{-2}				TACK, Kg cm^{-2}		TACK, Kg cm^{-2}		TACK, Kg cm^{-2}				
	NOT HEATED	HEATED	NOT HEATED	HEATED	NOT HEATED	HEATED	NOT HEATED	HEATED	NOT HEATED	HEATED	NOT HEATED	HEATED	
PLY-WOOD	6.5	9.0	9.1	9.6	18.	2.8	15	26	24	19.7	>22	27	EIGHT HOURS POLYMERIZATION PRODUCTS
CARDBOARD	12.9	6.8	>20	18	>16	9.2	20	9.2	25	27	>26	23	
GLASS	8.5	10	>15 Yeild-ed	>17 Yeilded	>15 glass Yeild-ed	6	7	9	134	>14	5.9	8.6	
ALUMINIUM	Nobond	Nobond	Very Weak bond	≈2.4	2	6.5	4	4.9	3	6	2	8.0	
TITANIUM	Nobond	Nobond	Nobond	Nobond	Nobond	Nobond	Nobond	Weak bond-age	Nobond	≈2	≈2	≈3.1	
PLYWOOD	8.9	15.6	18.7	6.7	220	>25	>192	>21.4	>23	>22	>18	>22	ELEVEN HOURS POLYMERIZATION PRODUCTS.
CARDBOARD	>18	>1	16.3	18	21.6	>28.1	>23	>25	10	>21.4	19.3	>32.0	
GLASS	Nobond	5.4	10	>15 Glass yeild-ed	14 Yeild-ed	>16 Yeilded	19 Yeild-ed	6.0	9	>17	>14	slippy	
ALUMINIUM	Nobond	≈1	Nobond	≈1.5	Nobond	≈1	≈1.5	≈3	weak bond	4.2	Nobond	weak bond	
TITANIUM	Nobond	≈2	Nobond	≈3	Nobond	>2	Nobond	>1	Nobond	Nobond	Nobond	Nobond	

ADHESION OF POLY(VINYL ACETATE) ADHESIVES WITH DIFFERENT AMOUNTS OF DIVINYL BENZENE USED AS FOR CROSS-LINKING AGENT.

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C O N C L U S I O N S

From the various observations and results of this study the following conclusions have been made.

1. Emulsion polymerisation for the production of poly(vinyl acetate) containing cross-linking agent, DVB, of different quantities must be carried out for a period of not less than 8hrs at 60°C. Products of shorter periods of polymerisation had not shown as high mechanical and adhesive properties from the tests performed with them, as had been obtained for the 8hr and 11hr polymerisation products.
2. Emulsions of PVAc, with and without cross-linking in the system, are good for bonding wood and paper (card-boards), and glass, where solutions of purified samples are not available. Plasticisation was found to improve the bonding strengths of the emulsions.
3. It was found that mechanical properties of purified PVAc films are dependent on solvent from which the films are cast. Extent of cross-linking of the polymer sample and plasticisation were also found to greatly affect the mechanical and adhesive properties of PVAc.
4. Plasticisation improves the elongation of polymer films if cast from certain solvents e.g. benzene and chloroform but generally weakened tensile strength and adhesion especially when the polymer is cross-linked.

5. Cross-linking of PVAc with different amounts of divinyl benzene had shown that products of such reaction show improved mechanical and adhesive properties. It was found from the tests conducted that cross-linking has a limit of advantage beyond which the mechanical and adhesive properties of PVAc produced deteriorated.
6. The type of treatment that would ensure high bondage in substrates was found to be greatly dependent on: type of substrates to be used, the type of adhesive, with regards to extent of cross-linking, and the after-joining treatments of the bonded substrates.
7. Titanium is best bonded with uncrosslinked polymer in the cold. If heat-treatment desirable, up to 5hrs heating at 100°C would produce the best results with PVAc adhesives, whether cross-linked or not.