SOME STUDIES ON THE ADHESIVE PROPERTIES OF POLYVINYL ACETATE

A Thesis
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in the Faculty of Science.

By
OGABA PHILIP OBANDE

Department of Chemistry
Ahmadu Bello University
Zaria Nigeria

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TO

My Wife

Oluwatoyin Pauline Obande

(to whom a great deal is owed)

SYNOPSIS

Emulsion, suspension, and solution techniques have been used to produce polyvinyl acetate having different degrees of branching and different molecular weights. Adhesive tests on lap joints formed with the aqueous suspension of the polymer, and the isolated purified and redissolved polymer revealed that the redissolved polymers have better adhesion than the aqueous suspensions. Tests using wood, glass, and metals showed the adhesion of the polymer to these materials to be excellent.

The effects of molecular weight and branching on the adhesion of the polymer revealed that the branched, low molecular weight polymer (not exceeding about 5×10^4) gave better adhesion than the more linear, higher molecular weight polymer.

Heat treatment of the adhesive joint was found to greatly improve the bond strength of the adhesive. It was found from the various results that the heat and water sensitivity of the polymer can hardly be improved by increasing the molecular weight or by cross-linking without reducing the adhesive properties of the polymer. A proposal has been made to resort to co-polymerization in-order to obtain a more heat and water resistant polymer.

A suggestion has also been made that polyvinyl acetate adhesives could be more economically produced by solution polymerization in some selected solvents and used without isolation.

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Erratum

All references to tack should be understood to mean bond strength.

CHAPTER 1

1.0 INTRODUCTION

Polyvinyl acetate (PVAc) resins find wide uses as surface coatings, adhesives, and binders in various forms. Of primary importance in these applications is the resin's ability to bind to other materials. Its binding to wood, metal, glass, leather, textiles and ceramics (including concrete) has been found to be good (1).

However, the present vinyl acetate polymer products have a number of faults which are often overlooked because of low costs. The aqueous dispersions have poor wet-tack, the films are water sensitive, brittle at low temperatures and turn yellow on heating. Methods such as co-polymerization and plasticization have been used to overcome these disadvantages but such developments have their own disadvantages - co-polymerization raises costs and additives do not only increase costs but also decrease some important properties such as water and heat resistances of the film. Hence the need for more studies.

This work aims at synthesising vinyl acetate polymer under different conditions to obtain materials of sufficiently different molecular properties (in particular molecular weight and branching), and studying some parameters of the polymer products which are known to influence the behaviour of the processed material. Such parameters include binding properties, mechanical properties of films, film sensitivity to heat and water, and variations in the minimum film

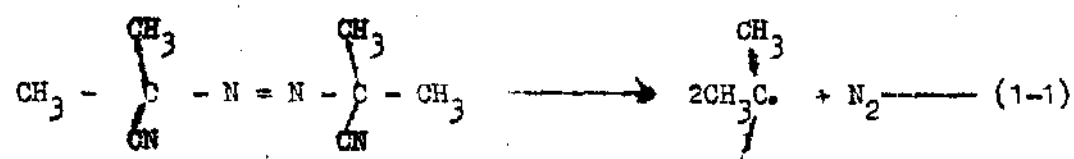
formation temperature with molecular properties. An attempt has also been made to study the influence of polyvinyl alcohol (a common component of resin formulations) on some of these parameters.

The purified polymer was 'characterised' and used without fractionation because of the desire to follow the behaviour likely to result from the use of most commercially produced resins since these are often marketed unfractionated. Although the views of Wagner (45) on such a practice are highly regarded it is felt that the practice reveals more of what the consumer obtains from using the marketed products than a study using well fractionated samples.

1.1 General Aspects of Free-Radical Polymerization (2)

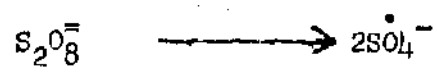
1.1.1 Chemistry of Vinyl Polymerization

A free-radical may be defined as a chemical fragment possessing an odd or unpaired electron. Examples being the reactive dimethylcyanocarbinyl radical obtained from aliphatic azobisnitriles:



(1-1)

and the sulphate ion radical obtained from the decomposition of persulphates:

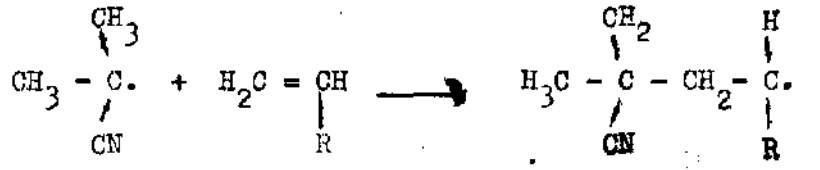


(1-2)

the free-radical-initiated polymerization process is generally

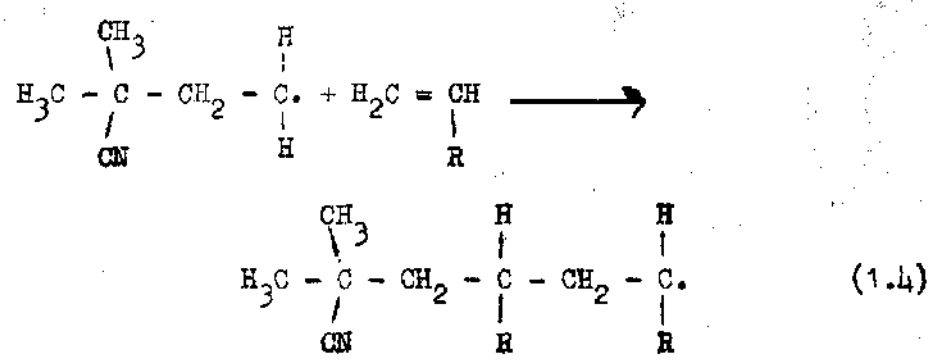
limited to forming macromolecules from monomers possessing olefinic links. The process can be separated into four steps:

(a) Inhibition: formation of radicals by the decomposition of the initiator as in equations (1-1) and (1-2) above and an attack of the radical on a monomer molecule:



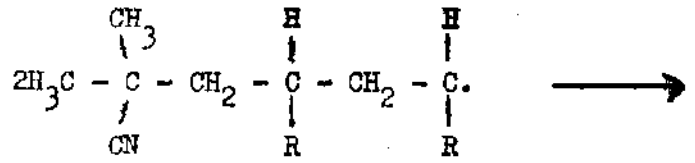
(1-3)

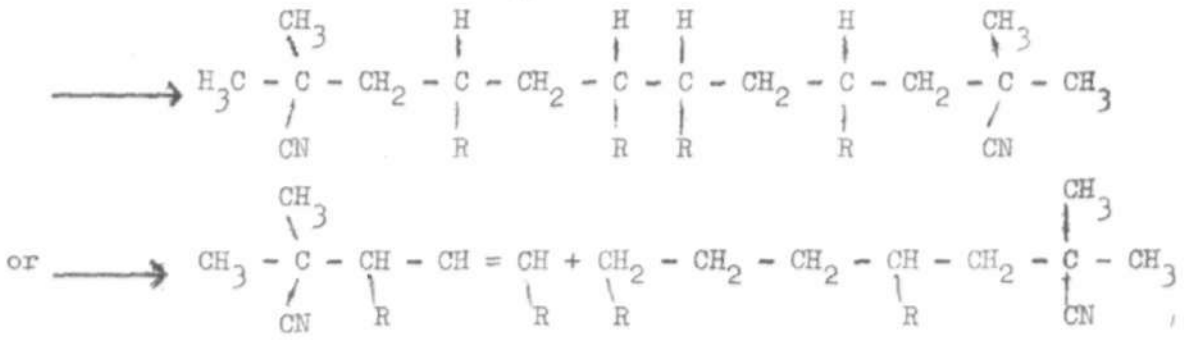
(b) Propagation: Successive addition of monomers to the growing chain radical:



(1.4)

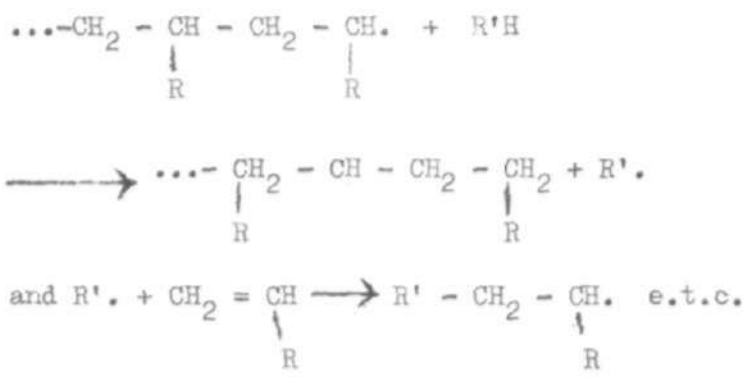
(c) Termination: recombination or disproportionation of the chain radicals to produce dead chains:





(1.5)

(d) Chain transfer: the activity of the chain radical is transfered to the solvent, the polymer, the monomer, or a transfer agent, R'H



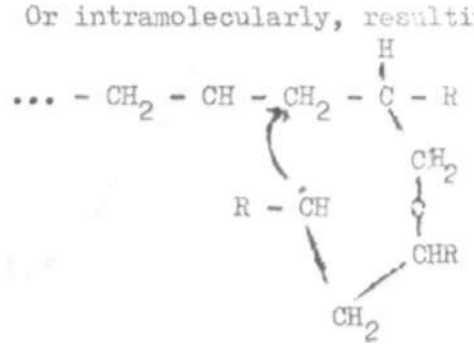
(1.6)

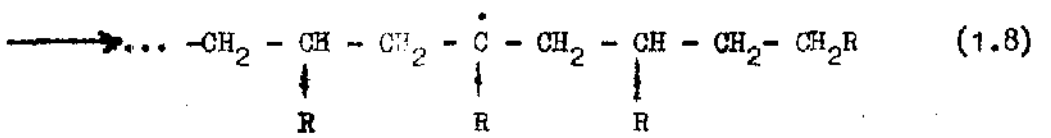
Branching results from transfer to polymer. Radicals may transfer intermolecularly resulting in long chain branching:



new chain radical (1.7)

Or intramolecularly, resulting in short chain branching:





(1.8)

Mayo (3) using published data on styrene polymerization related the average degree of polymerization, $\bar{DP}$, to the transfer constant, C_s, defined as the ratio of the rate constants for the transfer, [redacted] k_t, and propagation, k_p, reactions, as follows:

$$1/\bar{DP} = C_s \frac{[S]}{[M]} + 1/\bar{DP}_o \qquad (1.9)$$

where $\bar{DP}_o$ = average degree of polymerization obtained when only pure monomer was polymerized,

$\bar{DP}$ = average degree of polymerization obtained in the presence of a solvent,

$[S]$ = moles of solvent, and

$[M]$ = moles of monomer.

1.1.2 Inhibition and Retardation

Free-radical initiated polymerization is subject to inhibition and retardation. Substances that can act as retarders include stablized radicals capable of reacting with other radicals but incapable of reacting with monomers. Thus, if the retarder reacts with a growing chain, it acts as a typical chain-transfer agent:

$$\ldots - P\cdot + X\cdot \longrightarrow \ldots - P + Y\cdot \qquad (1.10)$$

where ... -P· = growing polymer chain

X· = stablized radical or retarder

... -P = dead polymer chain

and Y· = stabilized product from X.

Inhibitors are chemical substances that cause well-defined induction periods, whereas retarders remain active throughout the whole course of polymerization. Both the inhibitors and retarders react with the initiating radicals to form new radicals which are took weak to initiate chain growth; but the inhibitors react rapidly whereas the retarders react only slowly. The retarders can also react with the growing polymer chain to be chain terminators.

1.2 The Mechanism of Vinyl Acetate Polymerization

Vinyl acetate can be polymerized by all known methods of polymerization - bulk, solution (4,5), suspension (6-8), and emulsion (9-11). The mechanisms being principally free-radical and redox polymerizations. Initiators which are known to react with vinyl monomers usually by ionic mechanisms have been found to react with vinyl acetate usually by free-radical mechanism (12-15). The scheme of reaction is described in Section 1.1.1 above.

1.2.1 Solution Polymerization

The solution polymerization mechanism is mainly determined by the type of solvent employed. The solvent will influence the final molecular weight (17), by acting as a chain transfer agent, and the nature of the polymer end-groups. The nature of this influence depends on the solvent transfer constant (16). Polymerization of vinyl acetate in solution is known to be very sensitive to the presence of impurities and the influence of several impurities in the commercially available monomer on polymerization has been widely studied (17).

1.2.2 Emulsion Polymerization

The Smith-Ewart theory (19) which is based on the work of Harkins (18), and further developed by Howard (20), stipulates that emulsion polymerization consists essentially of a system of water, a monomer that is water-insoluble, an emulsifier, and a water-soluble initiator which produces radicals when decomposing. At the early stages of an emulsion polymerization the system consist of monomer droplets (about $10^{10}/cm^3$), stabilized by the emulsifier molecules, decomposing initiator producing radicals, emulsifier micelles containing solubilized monomer (about $10^{18}/cm^3$), monomer-swollen polymer particles, and the continuous aqueous phase. Since there are many more micelles than monomer droplets the polymerization takes place essentially only in the micelles

and not in the droplets. The monomer in the micelle is used up rapidly but more monomer diffuse into the micelle (now swollen with polymer) from the monomer droplet through the continuous equeous phase until the monomer droplets disappear and the micelles have changed to polymer particles. After about 15-20% conversion no new micelles can be formed because the total surface area of the particles in the system increases and thus the emulsifier concentration in the aqueous phase is reduced to below the critical micelle concentration for the surfactant.

Smith and Ewart proposed a kinetic scheme consisting essentially of two cases:

1. The rate of exit or termination of radicals is much slower than the rate of entry. In this case the rate of polymerization can be described by the expression used for bulk polymerization:

$$R_p = k_p [M] (k_d [I] f/k_t)^{\frac{1}{2}} \qquad (1.11)$$

where R_p = rate of chain propagation

k_p = propagation constant

$[M]$ = monomer concentration

k_d = decomposition constant

$[I]$ = initiator concentration

f = initiator efficiency,

and k_t = termination constant.

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

$$dM/dt = R_p = k_p [M] [R.] \qquad (1.12)$$

where $[R.]$ = radical concentration.

Since there will be one radical per particle half the time equation (1.12) becomes:

$$R_p = k_p [M] (N/2) \qquad (1.13)$$

where N = total number of particles.

One of the important points of this rate equation is that an increase in the initiator concentration does not lead to an increase in the rate of polymerization, although it will affect the molecular weight. From equation (1.12) the molecular weight can be calculated assuming no transfer reactions take place. The rate of decomposition of the initiator is given by:

$$\rho = k_d [I] \qquad (1.14)$$

N/ρ gives the time of growth of a chain, and the molecular weight is equal to $k_p(N/\rho)$. Any increase in $[I]$ results in an increase in ρ and thereby reduces the molecular weight.

1.2.3 Suspension Polymerization

In suspension polymerization the monomer is mechanically dispersed in a liquid, usually water, which is a non-solvent for the monomer as well as for all the polymer species that are formed in the reaction. A suspension stabilizer is used to keep globules dispersed during polymerization. Monomer-soluble initiators are preferred so that they remain dissolved in the monomer droplets throughout the course of the polymerization. Benzoyl peroxide and azobisisobutyronitrile (AIBN) have been found to be more efficient than sodium persulphate which is soluble in water and not in the monomer.

The organic phase in a suspension polymerization exists in water in discrete microscopic beads throughout the whole reaction, before, during, and after polymerization with noticeable organic phase and a monomer/non-solvent interphase.

Often no difference in rates are found for suspension and for bulk polymerization. Kinetic data on suspension polymerization of styrene (21) show that initiation, propagation, and termination apparently all occur inside the pearl in the same way as in bulk polymerization.

1.3 Characterisation of Polyvinyl acetate by viscosity method

Solution viscosity is basically a measure of size or extension in space of polymer molecules. High molecular weight polymer molecules possess the unique capacity to greatly increase the viscosity of the liquid in which they are dissolved, even when present at low concentrations. It is generally known that the higher the moelcular weight within a given series of linear polymer homologs the greater the increase in viscosity produced by a given weight concentration of polymer. Thus, the intrinsic viscosity, which represents the capacity of a polymer to enhance the viscosity, increases with $\bar{M}_v$, hence viscosity measurements afford a measure of molecular weight. The relationship is only empirical but the method has found widespread use.

The experimental procedure consists of measuring the efflux time, t, it takes a given volume of solvent or polymer solution to flow through the capillary of a viscometer. The more popular viscometer used for studying viscosity of polymer solutions include Ubbelohde and zero-shear types.

Usually the efflux time is taken to be a valuable indication of the solution viscosity, η. Schulz (22) has related the efflux time, t, to the viscosity, η, by the expression:

$$\eta = \alpha\rho\,(t - \beta/\alpha t) \qquad (1.15)$$

where ρ = density of solvent (or solution) and (α, β) = caliberation constants.

The viscosity of the solution is divided by the viscosity of the solvent to obtain the relative viscosity, η_r. The specific viscosity, $\eta_{sp} = \eta_r - 1$, expresses the incremental viscosity attributable to the polymer solute. The ratio (η_{sp}/c) is a measure of the specific capacity of the polymer to increase the relative viscosity. The limiting value of this ratio at infinite dilution is called the intrinsic viscosity orlimiting viscosity, $[\eta]$, written as

$$[\eta] = (\eta_{sp}/c)_{c=0} \qquad (1.16)$$

The concentration, c, is expressed in grams per 100 cm^3 of solution, the intrinsic viscosity being given in the receiprocal of this unit, i.e. in decilitres per gram, dl/g.

Plots of (η_{sp}/C) against c are usually linear for $\eta_r \leq 2$, and it has been pointed out that the slopes of these plots for a given polymer-solvent system vary approximately as the square of the intrinsic viscosity. According to Huggins (23),

$$(\eta_{sp}/c) = [\eta] + k^1[\eta]^2 c \qquad (1.17)$$

where k^1 = approximately constant for a series of polymer homologs in a given solvent.

The molecular weight of the polymer may be obtained from the Mark - Houwink relationship:

$$[\eta] = KM^{\alpha} \qquad (.18)$$

where $[\eta]$ = intrinsic viscosity,

K and α = constants for a given solvent at a given temperature,

and M = molecular weight of polymer.

1.3.1 Viscosity measurement in the theta - condition

It is often more helpful to measure the viscosity of polymer solutions under a special condition known as the theta-, θ-, condition. Theta - solvents (θ - solvents) being defined as solvents in which, at given temperatures, a polymer molecule is in the theta - state. These temperatures are also known as theta, θ -, temperatures. In the theta-state, the solution behaves thermodynamically ideal at low concentrations. The theta-temperature being phenomenologically defined as the critical miscibility temperature at the limit of infinite molecular weight (40). Thermodynamically, it has been shown that the excess free energy of dilution at the theta-condition (θ - temperature and θ - solvent) is zero. Hence equation (1.18) above becomes:

$$[\eta]_{\theta} = K_{\theta}M^{0.5} \qquad (1.18a)$$

where $[\eta]_{\theta}$ = intrinsic viscosity obtained at θ - condition

K_θ = constant

α = 0.5

and M = molecular weight.

1.4 Plasticization of Principal Polymers

Polymers, in general, exhibit a temperature dependent property known as glass transition whereby there is a specific, or a narrow range of, temperature below which the polymeric material is glassy and brittle and above which it is rubbery and flexible.

The glass transition temperature of most principal polymers are about or well above ambient temperature, the actual value being dependent on the molecular weight of the polymer. For this reason most thermoplastic polymers have to be softened to make them serviceable at ambient conditions.

A plasticizer, therefore, is defined as a non-volatile low molecular weight substance (usually an organic liquid) which when added to a polymer softens it and makes it more flexible.

The theory of plasticisation has not received much attention, and the choice and mode of application of the plasticiser to a given system is based on the results of previous workers or on trial-and-error. In general, however, plasticisers are dry-blended with solid compoundates; for emulsions and suspensions, it is properly stirred into the hot emulsion and allowed sufficient time to diffuse into

the polymer; for solutions it is added to the solid polymer prior to dissolution or stirred into the polymer solution (24).

Of primary importance (among others) in plasticisation is compatibility, the plasticiser has to be sufficiently compatible with the polymer and must not migrate from the processed material under service conditions.

Dibutyl phthalate (DBP) has been found, among some other plasticisers to be suitable for polyvinyl acetate adhesives (24, 25), and 10% plasticiser, on total weight of resin has been found to be optimal (24).

1.5 The Theories of Adhesion

An adhesive is defined as a substance capable of holding materials together by surface attachment.

The actual mechanism of adhesive attachment is not yet very well defined. Various theories attempt to describe the phenomena of adhesion. Each theory contains points that are partially correct; and no single theory explains adhesion in a general, all-encompassing way. A knowledge of adhesion theories can, however, assist in understanding the basic requirements for a good bond.

The theories that have been advanced to explain adhesion include a mechanical theory, an adsorption theory, a diffusion theory, and an electrostatic theory.

1.5.1 The mechanical theory of adhesion

The original theory of adhesion is the mechanical one. This suggests that an adhesive is able to penetrate rough surfaces and form a mechanical lock. Thus adhesion is primarily governed by the mechanism of penetration of a liquid into capillaries, the depth of penetration, h, in time, t, being given by the Washburn equation:

$$dh/dt = r\lambda \cos\theta/4\eta h \qquad (1.19)$$

where r = diameter of capillary

λ = surface tension of liquid

θ = contact angle between the liquid and the solid,

and η = viscosity of the liquid.

The main variable is the viscosity and this is applied in practice by using either the adhesive in solution form, the solvent being lost by evaporation and/or adsorption, or alternatively, by the use of an adhesive which is capable of cure.

1.5.2 The Adsorption theory of adhesion

The adsorption theory states that adhesion results from molecular contact between two materials and the surface forces which result. For an adhesive to be effective, that is to approach the adherend at such a close range of operation of molecular forces, it is necessary that it wet the surface of the adherend properly. Complete wetting, that is with zero contact angle being desireable. The contact angle, θ, is a good inverse measure of wetting and spreadability, and hence of

adhesion. This is shown by the expression

$$W_{SL} = \lambda (1 + \cos \theta) \qquad (1.20)$$

where: W_{SL} = work of separation of solid and liquid surface

λ = surface tension of liquid.

1.5.3 The Electrostatic theory of adhesion

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 sub strate.

1.5.4 The diffusion theory of adhesion

The fundamental concept of the diffusion theory is that adhesion arises through the interdiffusion of molecules in the adhesive and adherend. The diffusion theory is primarily applicable when both the adhesive and adherend are polymeric, having long chain molecules capable of movement. The theory is based on mutual solubility of polymers. The limiting case is where the adhesive is dissolved in a solvent for the adherend for which the boundary between the two phases disappears in favour of a gradual transition from one polymer to another. The depth of penetration during diffusion need not be great.

On the basis of the diffusion theory, it has been shown that a highly branched polymer will have greater adhesion than an unbranched one, the adhesive strength of two non-polar polymers being directly proportional to (2/3) power of the number of effective branches (24).

The effect of molecular weight on adhesion is rather complicated, but it is known that diffusion falls off as molecular weight increases (24). However, since cohesive strength increases with molecular weight, there would be an optimum value in most cases for molecular weight.

A number of workers have stressed the importance of the hydroxyl group in adhesion (24). This is particularly noteworthy with polyvinyl acetate, which invariably contains some hydroxyl groups due to slight hydrolysis.

Most of these theories have been extensively reviewed by Voyutskii (26) and Zisman (27).

1.6 The Minimum Film Formation Temperature

The minimum film formation temperature (MFT) of a polymer is defined as the temperature below which the polymer in its latices or emulsions will not exist as a continuous film when coated on a surface.

The MFT value is often quoted as being synonymous with the glass transition temperature, T_g (24). The theory of glass transitions of polymers could, therefore, be said to be applicable to the MFT.

A number of descriptions of suitable apparatus for measuring the MFT of polymer latices and emulsions have been given (24). In this study an instrument was constructed according to the description by Warson (24). The measurement consists, essentially, of spreading the emulsion to be tested over a place across which a suitable temperature gradient is maintained. The film is allowed to dry and the MFT found by visual inspection at the point where the film becomes white and discontinuous.

CHAPTER 2

2.0 EXPERIMENTAL METHODS

2.1 Preparation of Branched Polyvinyl acetate

2.1.1 Materials and their Purifications

1. Hydroquinone stabilized vinyl acetate, reagent and commercial grades. Supplied respectively by the British Drug Houses, Poole, England, and the Nigerian Hoechst Ltd., Lagos, Nigeria.
2. Potassium persulphate, reagent grade
3. Sodium persulphate, reagent grade
4. Sodium lauryl sulphate, specially purified grade, and
5. Sodium dihydrogen phosphate, hydrated, reagent grade

All supplied by the British Drug Houses.

Both grades of vinyl acetate were purified by first washing thoroughly with 5% sodium hydroxide to remove the hydroquinone inhibitor, (complete removal being taken as the absence of any coloration on addition of the base). It was then washed with small portions of distilled water until free from the sodium hydroxide. It was then dried over sodium sulphate and fractionated using an all-glass Dufton column. The fraction $\angle_{\text{boiling}}$ between 72° and $72.5^{\circ}C$ was collected and stored under vacuo in a refridgerator. It was passed over silica column just before use.

Sodium (and potassium) persulphate were recrystallised twice from water, dried and stored over silica gel.

Sodium lauryl sulphate (specially purified) and sodium dihydrogen phosphate were used without further purification.

2.1.2 Methods

Suspension polymerization technique as reported by Sorenson and Campbell (29) was used but sodium (or potassium) persulphate was used as initiator instead of the suggested azobisisobutyronitrile since the former has higher transfer constant for polyvinyl acetate (2). Reactions were carried out at 40° and 70°C respectively in a thermostated bath capable of maintaining the temperature constant to ± 0.02°C. The summary of conditions used are shown in Table 3.1.1.

2.1.3 Experimental

A 2-litre four-neckedflask equipped with a controllable stirrer, an efficient condenser, a thermometer, and a monomer dropper, immersed in a constant temperature bath was thoroughly flushed with purified nitrogen. Under nitrogen atmosphere, 520 cm^3 of freshly distilled

water, 2_g of sodium lauryl sulphate, 2_g of sodium dihydrogen phosphate, and 3.5_g of recrystallised sodium (or an equivalent amount of potassium) persulphate were introduced into the flask. The water was purged by passing in nitrogen with gentle stirring. 200_g of purified vinyl acetate were gradually introduced through the monomer dropper under the nitrogen atmosphere.

Samples of the reaction mixture were withdrawn at various time intervals (see Table 3.1.1). The polymer was isolated and purified as described in section 2.3, below. The conversions were estimated gravimetrically.

2.2 Preparation of Polyvinyl acetate different Samples of Molecular Weights.

2.2.1 Materials and their Purification.

1. All materials in Section 2.1 except the persulphate initiators,
2. 2,2' - azobisisobutyronitrile (AIBN), (reagent grade)
3. Nitrobenzene (reagent grade)

All supplied by British Drug Houses.

AIBN was recrystallized from methanol. Its melting point was 100-102°C. Methanol and nitrobenzene were used without further purification.

2.2.2 Experimental Methods

Suspension and solution polymerization methods were used as reported by Sorenson and Campbell (29) and Ham [2], respectively.

A. Suspension Polymerization:

The procedure is basically as reported in Section 2.1. A 1 litre flask was used and the recipe consisted of 50$_g$ of vinyl acetate, 134 ml of water, 0.5$_g$ of sodium lauryl sulphate, 0.5$_g$, of sodium dihydrogen phosphate (dihydrate) and 0.5$_g$ of AIBN.

Various temperatures between 50 and 65°C were selected, 0.0167% and 0.0334% nitrobenzene on initiator (w/w) were used as retarders in some runs. The time of reaction was varied from 30 minutes to 24 hours to obtain reasonable yields. The results are summarised in Table 3.3.1.

B. Solution Polymerization

The same set-up as in A above was used. Methanol was used as solvent. The proportion of vinyl acetate to methanol (v/v) was varied from 1:1 to 1.3, 50$_g$ of monomer was used in each case and the amount of methanol varied to get the desired ratio. The initiator concentration was varied accordingly to compensate for slower reactions with increasing methanol concentration (2). The temperature was kept constant at 60°C throughout the runs. Isolation and purification of the polymer have been described below. The results are summarised in Table 3.2.1.

2.3. Isolation and Purification of Polyvinyl acetate prepared by Solution, Suspension and Emulsion polymerisation

It is surprising that sufficient attention does not seem to have been given to consious efforts to device methods of isolation and purification of polyvinyl acetate considering the need for high polymer purity required in most studies - including polymer characterisation.

An attempt to fractionate, or isolate and purify, the polymer from its reaction medium would likely encounter appreciable difficulties. Alfrey and Berdick (28) have attributed the difficulty in freeing the polymer from traces of monomer, catalyst, solvent, and other contaminating materials to the low softening point of the polymer, its excellent adhesion, ready solubility, and low apparent second-order transition. Sorenson and Campbell (29), quoting the works of several workers, suggested, invariably, that steam should be passed into the polymerization medium to drive off the unreacted monomer - after the desired extent of reaction - and the resulting polymer filtered in a sintered glass funnel by suction. They suggested that the polymer from solution polymerizations should be first broken up, and in one case that drying be done at 150°C .

It is the opinion of the author that suction helps the polymer to cohere to a hard mass during filteration. Also it is not easy to

break up the polymer freshly extracted from solution polymerization in most cases because of its sticky nature. Drying in the region of 150°C often leads to yellowing of the polymer (1).

Melville and Sewell (30), working on fractionated samples, described various ways of redissolution and reprec iptiation of the reacetylated polymer, after hydrolysis, using various solvent-non-solvent systems. They suggested the importance of added salts to the aqueous precipitant, when necessary, to improve the form of the precipitate. Frielander and his co-workers (31) in their studies on the stereo - regularity of the derived polyvinyl alcohol briefly described successive precipitations. Pinner (32) emphasised the use of dilute polymer solution and a large excess of precipitant. Dilute solutions are also essential for good fractionation otherwise large fractions are obtained (30). In a patent to Nippon Rayon C., Japan, Morikawa, and Miyao (33) suggest the passing of the emulsions through cation and anion exchange resins to remove the impurities.

A great deal of the time spent on this study was devoted to finding the means of obtaining very pure polyvinyl acetate. It is striking that without a foreknowledge of the works of Alfrey and Berdick (28) most of the methods used, and the observations made, by the author were completely identical with those reported by the two authors.

Important and comprehensive as the works of Alfrey and Berdick may be, the author is of the opinion that the additional observations and suggestions made below may be of no less importance - especially to those undertaking studies on polyvinyl acetate for the first time.

It was observed that isolation and purification of polyvinyl acetate from solution polymerizations were much more difficult than from some suspension and emulsion polymerizations. Whereas in the case of suspension and emulsion polymerizations isolation and purification were found to be dependent on the percentage conversion of the monomer to the polymer, there does not seem to be any factor controlling isolation and purification in the case of solution polymerization for which redissolution and reprecipitation seem to be the only means.

Large-scale (about 15$_g$) purification of polyvinyl acetate by successive precipitation, especially using hydrocarbons, is not only expensive - very dilute solutions and large excess of precipitant are required, and often the precipitant cannot be recycled even after several redistillations, like when benzene (or acetone), and petroleum e ther are used as solution and precipitant respectively - but very slow and tedious. Addition of solution to precipitant has to be dropwise (28) or in very thin stream (32). The speed of purification by redissolution and reprecipitation can hardly be improved upon without impairing the quality of the precipitates especially where small scale laboratory equipments are to be used for qus ntities of polymer over 20$_g$. Apart from the use of dilute solutions and manner of additions discussed above, other criteria for obtaining better precipitates include the use of high speed stirring, and the avoidance of vortex during stirring. These points were also emphasised by Alfrey and Berdick (28).

In view of the relatively higher costs of other solvents compared to water the author has outlined three methods of purification from aqueous precipitants below. None of the methods differs greatly from that described by Alfrey and Berdick, but the dependance on the technique of polymerization and the percentage conversion have been added as guidlines for chosing an appropriate method.

2.3.1 Purification of polyvinyl acetate obtained by solution polymerization

The polymer is isolated by precipitating it directly from the reaction mixture using a non-solvent for the polymer which is miscible with the solvent used for polymerization; a sticky material may result from this precipitation. The polymer is washed a few times in the precipitant and redissolved in suficient methanol, acetone, ethanol, or some other water-miscible solvent for it. The resulting solution is diluted batchwise to give a concentration of not more than 2_g polymer in 100 cm^3 solution of batch - the optimal concentration depends on the viscosity as also pointed out by Alfrey and Berdick. The diluted solution is then precipitated from a large excess of water in batches by dropwise addition. Vigorous stirring is reguired to obtain fine precipitate, vortex must be avoided while stirring, and the volume ratio of added polymer solvent to precipitant must not exceed about 1:5; a ratio of about 1:10 may be more effective but the upper limit depends on the viscosity of the solution. (28).

Sodium chloride (or sulphate) and/or a little concentrated hydrochloric acid may be added to the aqueous precipitant - their amounts

need not be quantitative. The need for added salt or acid depends on the relative purity of the dissolved polymer, the less pure the greater the need.

During batchwise precipitation the precipitates from batches are skimmed into sufficient quantity of pure water in a beaker. The polymer must not be pressed together en masse while handling and it must not be allowed to go dry during purification.

The filtered mass is washed several times by successively breaking it down in water which is vigorously stirred.

It is then filtered. When it is free from salt and/or acid, it is transfered to a large filter paper placed in a wide watch glass or some other flat container. It is broken down with the edge of a spatula and spread as much as possible then left to dry in the atmosphere overnight. It is then further broken down by grinding in a mortar and left to dry further in the atmosphere overnight. Finally it is vacuum dried at 55°-60°C for 24 hours with batches of silica gel in the oven to absorb excess moisture. Temperature control in this process is essential to avoid coloration of the sample. The product stores well and does not cohere on storage (28). Depending on the care taken in the purification process reasonably fine powders may be obtained with appearance similar to that described by Alfrey and Berdick.

It is, however, pertinent to mention that the use of hydrocarbon solvent and precipitant leads more easily to fine precipitates that dry

much faster and do not cohere on storage. The procedure should, therefore, be preferred when handling small amounts of polyvinyl acetate.

2.3.2- Purification of PVAc from aqueous polymerization products

When polymerization is carried out by emulsion or suspension technique, the method of isolation and purification of the polymer depends strongly on percentage conversion as shown below. It is suspected that the influence of adsorbed monomer, and the presence or absence of micelles play a major role in this respect among other possible factors.

The polymer is normally isolated from these polymerization systems by destabilising the soap by gradual addition of sufficient amount of acid or base while stirring (Section 2.3.1), or by the use of a solvent for the polymer which is miscible with water. However it was found that if these procedures are followed the form of the precipitated polymer may not be particulate as sometimes reported (29), depending on the conversion.

For conversions less than 20% when monomer absorption is still high and micelles probably still persist (6, 7, 9) the polymer comes out in a sticky form with highly occluded impurities which may be difficult to remove. Purification by successive precipitation as described in (2.3.1) above is recommended.

Between about 20 - 40% conversion may be regarded as intermediate and method (2.3.1) above or 2.3.2(A) described below may be used for purification, the applicable method will depend on the ease of isolation

as described in [redacted].2.3.1

(A). For about 40-70% conversion the polymer from the reaction medium may be diluted and directly precipitated from well stirred water containing some sodium chloride and/or concentrated hydrochloric acid. No redissolution may be necessary and batchwise precipitation yields better precipitate. All the former criteria outlined for 2.3.1 apply here too. After precipitation further purification is as described in the later parts of 2.3.1.

(B). When conversion is above about 70% purification is relatively easy. The suspended polymer is diluted with sufficient water and a small amount of sodium chloride is added with stirring. The polymer is then filtered and purified as described in the later parts of 2.3.1 Batches of about 20 g polymer can be conveniently handled by this method, and the resulting polymer is very similar in physical appearance to the polyvinyl alcohol (Mol.wt. 140,000) marketed by the British Drug Houses, except that the polyvinyl acetate is whiter. It does not cohere even on prolonged storage.

2.4 Determination of the molecular weight and the degree of branching of polyvinyl acetate by solution viscosity measurements.

2.4.1 Experimental

Materials:

1. Methanol - analytical grade
2. Ethanol - analytical grade

Both supplied by British Drug Houses. These were used without further purification.

Method:

The theta-conditions; θ - solvent and θ - temperature (section (1.3)) were used.

The polymer samples were dissolved in a mixture of ethanol and methanol, 60/40 (v/v) respectively[35]. Their solution viscosities were measured at 26.5°C using a Wilkens-Anderson (U.S.A) low temperature bath capable of maintaining the temperature correct to ± 0.02°C. The flow times were measured in an Ubelhode viscometer, with a solvent flow time of 90 seconds, immersed in the bath. A stopwatch with an accuracy of 0.1 second was used to record flow times.

2.4.2 Treatment of Data

Plots of $(\eta_{sp})/(c)$ against (C) were then made from the results of the flow-time measurements. Huggins' constant, k', was measured from the slope of each curve, and the moelcular weight of each

sample was calculated from the limiting viscosity $[\eta]$, using the relationship:

$$[\eta]_\theta = K_\theta \bar{M}_v^{\alpha} \qquad (1.18)$$

where: the values of K_θ and α are 101×10^{-5} dl/g. and 0.5 respectively (35), and $\bar{M}_v$ is the viscosity average molecular weight.

2.5 Preparation and Testing of Polyvinyl acetate Adhesives

2.5.1 Experimental

The adhesive samples were prepared by dissolving 2_g of polymer in 15 cm^3 of a mixture of acetone and methanol $^1/_{2.33}$ (v/v), respectively, in 50 $^{cm^3}$ stoppered conical flasks. Plasticization was done by adding about 10% dibutylphthalate (DBP) based on total weight of polymer (24), prior to addition of the solvent mixture. The polymer samples so prepared were left overnight under gentle agitation in a water bath equipped with a shaker and maintained at about 45 ^{o}C .

Strips of wood, glass, or metal, specially prepared were coated with the adhesive solutions. The area of coating being (2.5 x 1.0) cm^2. The coated substrates were allowed to dry sufficiently and the two strips joined together as shown in the diagram below. The lap-joint so formed were pressed together using a constant force of 5 k_g weight for 15 minutes, allowed to dry in the atmosphere for 72 hours, and tested with an Instron Tensile Tester with

a strain rate of 50mm/min. At a constant temperature and relative humidity of 20 ± 1.0°C and 24% respectively. The force of separation was divided by the area of application to obtain the tack.

2.5.2 Preparation of substrates for Adhesive joints (Adhints) (36)

1. Wood

The wood for adhints were plywoods supplied by the Sapele Plywood Industry, Sapele, Nigeria. The veniers of a sheet of plywood were trimmed off to obtain two-plies only. Strips measuring 6 x 1.0 cm were then cut out and an area of $(2.5 \times 1.0)cm^2$ marked off from one end of each strip. These marked out areas were sandpapered (in the direction of the grain) with medium grit sandpaper and finally solvent-cleaned with tissue paper soaked in purified toluene.

2. Glass

Non-corrosive microscope slides supplied by Teget Industries were cut into strips of 6.0 x 1.0 cm and an area measuring $(2.5 \times 1.0)cm^2$ etched from one end of each strip. The marked off area were sand papered and cleaned as described for wood.

3. Metal (aluminium and zinc strips were used)

The metal sheet was first scrubbed with moistened commercial 'vim' and thoroughly washed and dried. A face was then sandpapered with a 100 grit emery cloth. The sheet was cut into 6.0 x 1.0 cm strips.

An area measuring (2.5 x 1.0)cm^2 was marked off from one end of each strip with a knife edge. The strips were degreased by boiling in toluene and dried.

Metal strips so prepared were used immediately. The cleaning procedure was repeated after prolonged storage or for reuse.

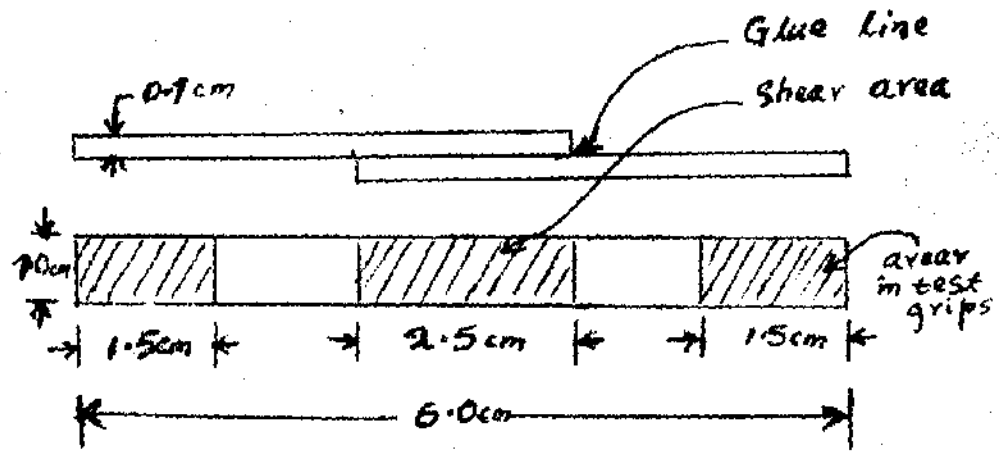


Fig. 2.1

Form and dimensions of lap-shear test specimen

2.6 Casting of films of Polyvinyl acetate and those of polyvinyl acetate/polyvinyl alcohol blends and the study of their mechanical properties.

2.6.1 Casting of films of PVAc

The polymer solutions were prepared as described above. Plasticization was similarly done and the plasticizer content was varied as desired.

The films were cast by measuring about $15cm^3$ of polymer solution on to clean mercury surfaces kept in small clean desiccators placed in a fume cupboard.

The solvent was allowed to slowly evaporate in the fume cupboard. After the solvent had evaporated the cast films were removed by cutting with a blade. They were allowed to dry further under vacuum over silica gel in desiccators at room temperature.

2.6.1 Mechanical Testing of films

Strips measuring 6.0 x 1.0 cm were cut out of each film and used for tensile testing using an Instron machine. The initial guage length of each strip being 2.5cm. The strain rate was kept constant at 50mm per minute, and measurements were carried out at constant temperature and humidity of $20^{o}C$ and 24% respectively.

2.6.3 Polyblending of polyvinyl acetate (PVAc) and polyvinyl alcohol (PVA)

Binary mixtures of PVAc and PVA were dissolved in dimethyl sulphoxide at $40^{o}C$. An attempt was made to cast the films over mercury

as above but it failed because the polymers tended to separate on evaporation of the solvent resulting in badly disfigured films.

2.6.4 Water absorption property of films

Films were cut into 5.0 x 2.5cm dimensions, weighed, and immersed in excess of distilled water in 100cm^3 beakers kept in a constant temperature and humidity room as above. After the absorption of water was thought to have attained equilibrium - in a period of one week - the films were removed, the ecess water wiped from their surfaces and they were weighed. No trend was observed using samples B_1 to B_7.

2.7 Heat treatment of Polyvinyl acetate Adhints

Sample B_1 was used to prepare adhints as described in Section 2.5.1 above using zinc strips. Sets of five adhints were successively heat set at 40°, 70°, 100°, 130° and 160°C, a set was left at room temperature as control. Each heat setting was done for 3 hours.

The adhesive strength of each set was measured using the Instron machine. The force of separation was divided by the area of application of the adhesive to obtain the tack value. (See Table 3).

2.8 Measurement of minimum Film Formation Temperature of films

The constructed instrument did not prove successful when an attempt was made to use it for this measurement.

CHAPTER 3

RESULTS AND DISCUSSIONS

3.0 The adhesion of PVAc, from aqueous suspension and from solution, to wood, glass and metals.

Table 3.0 shows the results of the measurement of adhesion using the polymer directly from the aqueous phase polymerizations, and the redissolved purified polymer from the same preparations.

The results show that the polymer in aqueous suspensions are much less affective as adhesives than when isolated, purified, and redissolved before application.

The poor adhesiveness of the aqueous suspensions compared to the solutions may be primarily due to the bead-like structure of the polymer when prepared in an aqueous phase. Such a structure permits only limited contact between the polymeric adhesive and the surface of the adherend. And from the theories of adhesion in Section 1.5, wetting is poor, diffusion is low, therefore the forces operating between adhesive and adherend are limited, resulting in poor adhesion. In addition to the limited contact between the polymer and the adherends is the fact that it is more difficult for the polymer particles in aqueous media to form a continuous film when dried between the plates of the adherends than when applied in solution forms. A discontinuous film between the plates of the adherend will obviously result in poor mechanical strength of film and therefore lower tack.

A second feature which may be observed from Table 3.0 is that in whichever form the adhesive is applied its bonding to wood is much better than its bonding to either glass or metals. This would normally be expected since wood is porous. It absorbs the applied polymeric paste into its pores leading to the formation of mechanical locks, and greater surface area of contact between adhesive and adherend (Section 1.5). The net effect is higher tack values.

It may be necessary to add here that in most of the tests the adherend material yielded before the polymeric adhesive. This was particularly the case with glass which yielded whenever the applied force exceeded 10 $kg.cm^{-2}$. It could, therefore, be concluded that the polymer has excellent adhesion to these materials.

3.1 Variation of the Huggins' constant, k', and the limiting viscosity, $[\eta]$, with conversion and molecular weight

The results of the determinations of the viscosity of dilute solutions of PVAc having different conversions prepared at 40° and $70^{\circ}C$ are shown in Table 3.1.2 and illustrated in Figs. 3.3 and 3.4, respectively.

3.1.1. Variation of $[\eta]$ and k' with conversion:

Fig. 3.3 shows that at $40^{\circ}C$ there is a continuous decrease in $[\eta]$ as conversion increases from 30% to about 100%. At $70^{\circ}C$, however, a sharp rise in $[\eta]$ is observed with conversion, a maximum is reached at about 70% conversion followed by a sharp fall.

In Section 1.3 it was explained that the limiting viscosity is the value of the ratio (η_{sp}/c) when c becomes zero. The ratio (η_{sp}/c) being the specific capacity of the polymer to increase the relative viscosity. The quantity (η_{sp}/c) should, therefore, increase with molecular weight and/or branching as reported by Melville (37).

The behaviour, and therefore structure, of polymer chains in solution is dependent on the hydrodynamic interactions of the dissolved polymer and the solvent molecules (35). When only the polymer molecules and the solvent molecules are present in solution these interaction are between polymer - polymer, polymer-solvent and solvent-solvent only (40). For the polymer chains to enhance the viscosity of the solution, that is, for the viscosity to increase with increase in the number of chain segments per polymer molecule, the polymer-solvent interaction has to be more favoured than the other interactions. The relative increase in viscosity caused by an increase in the number of chain segments will then follow the predicted value from equation (1-18). Any factor, therefore, which reduces the polymer-solvent interaction will lead to a reduction in the viscosity of the polymer solution regardless of any change in the number of segments in a chain of the polymer molecule.

Several workers have shown that branching occurs when polyvinyl acetate is polymerized to high conversions (30,37,46-48). The effect of conversion on the viscosity of the polymer solutions here would, therefore, mean the effect of branching. Indeed the viscosities of the

solutions were measured in an attempt to estimate the relative degree of branching in the prepared samples as is sometimes practiced (37).

It is apparent from the above discussions that branching could influence the viscosity of the dilute polymer solution. The extent of this influence would depend on the nature of the polymer chains in solution.

At 40°C chain transfer reactions are slow but long kinetic chains are produced (2,41). The results is that both the backbone chains and the side branches are long. The tendency of such long chains, present in solution, is not only to cause entanglement but also to coil up, especially when they are made to exist in their unperturbed states as in the theta-conditions used here (40). This tendency will be particularly strong with chains having bulky end-groups such as the sulphate group from the initiator. Thus the greater the number of such long chains per molecule of the polymer the more the tendency for the molecule to coil up and the greater the reduction in viscosity. It must be added that entanglement of the chain molecules will similarly reduce the viscosity since the greater the degree of entanglement the higher the probability of finding two segments in a given unit of volume of solution (40).

At 70°C, however, a different kinetics operates for both the propagation and transfer reactions (Section 1.1.1). Although both reactions are fast and competitive, only relatively short chains are produced (2,41). Such short chains are believed to have very little tendency to coil or entangle since they are not sufficiently bulky and

are too short to properly embrace one another in a medium which forces them to exist in the unperturbed state as in the theta-condition. The result is that hydrodynamic (polymer-solvent) interactions are favoured and viscosity increases with conversion as more side chains add to the backbone chain increasing the interactions. The increase in viscosity is observed up to about 70% conversion after which excessive branching causes the chains to become sufficiently bulky to coil and entangle. This reduces the viscosity. This reduction is large for all the samples prepared beyond about 90% conversion at both temperatures.

These observations and reasonings agree perfectly with the findings of Gillespie (39) who made similar studies. It would appear therefore that the deviation from the results of Melville (37) must be due to some differences in the structures of the polymers used for the different studies.

3.1.2 Dependence of $[\eta]$ and k' on molecular weight.

The results in Table 3.3.2 show a general decrease in $[\eta]$ with decreasing molecular weight as would be expected for linear flexible polymers. The values of k' fall within the range predicted by Flory (40). The higher values of k' for samples B_3 and B_4, and B_5 to B_7 are attributable to the effect of chain transfer action of nitrobenzene and methanol respectively. The increase from B_3 to B_4, and from B_5 to B_7 are due to the increasing concentration of these transfer agents. A decrease was not observed probably because the branching was not sufficient to cuase significant compacting of the chain as explained previously.

3.2 Dependence of the adhesion of PVAc on the extent of conversion.

The results of the adhesion tests on the samples prepared to different conversions (A_1 ~ A_{12}) are shown in Table 3.2 and illustrated in Fig. 3.5.

Fig. 3.5 shows that the tack passes through a maximum with increasing conversion at both temperatures. Since diffusion may not be considered as making much contribution to adhesion on the surface of a highly polished metal, this observation may be explained on the basis of the adsorption theory (Section 1.5.2). This theory basically 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. Equation (1-20) expresses this relationship quantitatively. For maximum contact between the adhesive and the substrate, the contact angle, θ, must be low, zero contact angle being most preferred. This also requires that the viscosity of the polymer solution be low.

It has been shown in the preceding section that the viscosities of the polymers prepared at 40°C are controlled by the coiling and entangling of the long chain branched polymer molecules in solution. Whereas viscosities of the samples prepared at 70°C are controlled by the quantity of short chain branching.

At 40°C the increase in tack with conversion is sharp because of the decreasing viscosity coupled with the net increase in the number of chain segments capable of participating in interaction of molecular forces between the polymer film and the substrates.

At 70°C, however, though the number of chain segments capable of participating in surface attachment with the substrate increases as more chain segments are added to the polymer molecule with conversion, the resultant increase in viscosity reduces adhesion, equation (1-20). Hence a more gentle rise in tack is obtained. The values of tack in this region (i.e. at low conversions) is higher at 70°C than at 40°C because of the greater number of chain segments capable of participating in interactions of molecular forces with the substrate at the higher temperature. This follows from the brief kinetic analysis of the polymer synthesis at the two temperatures and the behaviour of the resultant chains *in solution given previously in Section 3.1.1 above.*

At the turning point the effect of increased coiling and entanglement of chain segments becomes more pronounced at both temperatures. The net number of available chain segments for adhesion reduces and the measured tack is subsequently lowered. The reduction of tack beyond this point for samples prepared at 70°C is much more prominent than for samples prepared at 40°C. So that the order of tack values for both sets of samples is reversed. The samples prepared at 70°C have much lower tack values than those prepared at 40°C at the higher conversions. The reason for low tack values in this region is not only due to the reduction

in the number of effective chain segments caused by coiling but also to the reduction in intermolecular forces as coiling of chain segments becomes predominant. Such a reduction in interchain forces reduces the mechanical strength of the adjoining polymer film between the adherend plates. The effect is more pronounced with the samples prepared at 70°C because short chains are less likely to assume favourable random orientation that would enhance intermolecular attration. This is not the case with a randomly coiled long chain which could, more probably, contain regions along the chain length that are properly orientated to facilitate intermolecular attractions. Hence much higher values of tack are observed for samples prepared to high conversions at 40°C than at 70°C.

3.3 Dependence of the adhesion of PVAc on the molecular weight

The results of adhesion tests on samples of PVAc prepared to different molecular weights are shown in Table 3.3.3 and illustrated in Fig. 3.6.

Fig. 3.6 shows a general decrease in tack with increasing molecular weight in the region studied (10^4-10^5). For a given weight concentration of polymer the higher the molecular weight the greater the increase in viscosity (40) and hence the lower the tack of the adhesive to the adherend as explained above (Sections 3.1 and 3.2). But differences in viscosity alone cannot explain the very large difference in adhesion especially between the molecular weights of 10^4 and those of 10^5.

Considering the polymer alone, the longer the chains (that is the higher the molecular weight) the more likely side groups neutralise one another by engaging in secondary bondings. Although this will make the films tougher, it will reduce the number of polar side groups available for interaction of molecular forces with the adherend plates. The results is a reduction of adhesion with molecular weight.

In addition to the effect of the mutual cancellation of polar groups, the high molecular weight polymers are more brittle than their low molecular weight analogs. This is supported by the quantitative treatment proposed by Brysdon (50) for the relation between the glass transition temperature of polymers and their molecular weights; the treatment by Ferry, William, and Stern (43) relating the free volume to the polymer molecular weight; and the treatment by Rouse (42) relating the steady state shear compliance of the polymer to the molecular weight. All the literatures cited predict a decrease in the elastic modulus of the polymeric material with increasing molecular weight of the polymer. Such a decrease in the modulus will of course result in decreased tack as observed.

It may be relevant in this regard to draw attention to the striking resemblance in trend between Figs. 3.5 and 3.9a and 3.9b. Also the patterns shown in Tables 3.2 and 3.3.3, and Tables 3.6.1 and 3.6.2, respectively, indicate unequivocally, that the adhesive strength of the polymer is solely dependent on its elastic properties - that is the yield stress and the tensile modulus - and independent of the ultimate tensile

strength. So that although the ultimate tensile strength increases with molecular weight (40), the elastic properties decrease with the molecular weight (42, 43, 50). Hence adhesion decreases with molecular weight for high molecular weight PVAc in the region of 10^4 and above.

Florea (44) working on a similar study as above with some group observed an increase in adhesion with molecular weight up to a limit beyond which further increase in molecular weight did not result in any increase in adhesion. Their results suggest a study using lower molecular weight polymers than were used in this study, hence the results here may be complementary to their results.

It would be expected, therefore, from the results here and those of the previous workers that the increase in tack observed for decreasing molecular weight will reach a constant value at some point most probably between molecular weights of 10^3 and 10^4. Beyond this point any further increase in molecular weight will result in reduced adhesion.

3.4 Effect of Plasticization with dibutyl phthalate, DBP, on the adhesion of PVAc

Fig. 3.7 illustrates the results of adhesion testing on high molecular weight (B_2 and B_1) and lower molecular weight (B_6 and B_7) samples of PVAc shown in Table 3.4. Equal concentrations of the polymer samples were dissolved and used for the tests.

It is apparent from Fig. 3.7 that as the plasticizer content is increased step-wise from zero to 30% DBP, the value of tack for each

sample passes through a maximum at about 10% DBP and decreases to values about the unplasticized samples at 30% DBP.

These results have been compared to those for the study of the mechanical properties of the polymer films reported in Table 3.6.2, and illustrated in Figs. 3.10 and 3.11. It would be seen from Table 3.6.2. that as the plasticizer content of a given sample increases from zero through 20%, the elastic modulus decreases sharply from very high values in the absence of any plasticizer to very low values in the presence of the limit of 20% plasticizer investigated. Fig. 3.10 shows that the tensile modulus decreases linearly with molecular weight only around 10 - 15% plasticization, and Fig. 3.11 shows that the lower molecular weight are much more sentive to plasticization than the higher molecular weight analogs.

The above points, and the effect of viscosity discussed in Sections 3.2 and 3.3 easily explain the trend observed for tack in Fig. 3.7. The adhesion is low in the absence of any plasticizer because the polymer is too brittle, and hence it is not only more difficult for it to make good contact with (or wet) the surface of the adherend, but it also has poor mechanical strength.

As the plasticizer content is increased from 5% to 10% the value of tack rises due to the improved softening of the polymeric material leading to more efficient contact between the adhesive and the adherend. The result is greater interaction between the substrate and the adhesive film.

Although the modulus is reduced, Figs. 3.10 and 3.11, the reduction is greatly compensated for by the improved wetting of the surface of the adherend by the adhesive. So that the value of tack at 10% DBP is higher than the value at 5%.

Above 10% plasticizer content, both tack and modulus decrease very rapidly. The polymer becomes too soft to have any useful mechanical and adhesive qualities. Fig. 3.11 reveals this more clearly in showing the sharp reduction in modulus after 15% plasticization for the higher molecular weight series (B_2, B_0 and B_1) and after 10% for the lower molecular weight series (B_6 and B_7).

The higher molecular weight species have lower tack for the same reasons as discussed in Section 3.3. They are also less sensitive to plasticization as would normally be expected and as revealed in Fig.3.11.

In conclusion, therefore, about 10% dibutyl phthalate seems to be an optimal amount for the plasticization of polyvinyl acetate adhesives. The plasticized polymer has enhanced adhesive properties and the decrease in elastic properties does not have much impact on the enhanced adhesion.

3.5 Effect of heat treatment on the adhesion of PVAc

The result of heat treatment of adhints formed by using sample B_1, plasticized with 10% DBP, are shown in Table 3.5 and illustrated in Fig. 3.8.

A general rise in tack is observed when the adhesive joint is heat treated. The rise is sharp between 25° and 40°C because the plasticized polymer softens in this region (T_g of pure PVAc = 28°C (24)), and the softened polymer makes better contact with the substrate.

Between 40° and 130°C the increase is gradual. In this region there is increased softening and complete evaporation of the absorbed/ adsorbed solvent. Any gas trapped between the adhesive and the adherend are also released. The net effect is better contact between the adhesive and the substrate leading to greater adhesion.

Between 130° and 160°C there is a sharp rise probably due to the fact that the plasticized polymer might begin to melt in this region. The molten, or extremely softened, polymer completely wets the surface of the adherend, especially as trapped gas are absent or very few. Since no degredation has taken place (shown by the absence of any coloration of the film after testing), very high value of tack results.

The study was not carried beyond 160°C, however, it would be expected from the observed trend that as the heat setting temperature of the adhesive joint increases, keeping the time of heating constant, the

adhesiveness of the polymer will increase. This will be so only upto the temperature at which the polymer begins to degrade. At this temperature, and beyond it, the mechanical strength of the degraded product might not be sufficient to allow formation of a good bond. So that for PVAc the tack might increase even above 160°C, probably upto about 180° to 190°C just before degredation sets in around 200°C as reported by Jenkins (49).

In conclusion, for bonding with PVAc adhesives, heat treatment of the adhesive joint, where possible, leads to highly improved bond strength if duration and temperature of heating are carefully selected. The maximum temperature to which heating can be done, within a given length of time, without degredation would of course depend on the molecular weight of the polymer. Since usually, the higher the molecular weight the higher the degredation temperature (51).

3.6 Effect of plasticization, branching, and molecular weight on the mechanical properties of PVAc films

3.6.1 Plasticization

The effect of plasticization on the mechanical properties of PVAc films was briefly discussed in Section 3.4. It would be seen from Table 3.6.2 that plasticization generally softens the polymer as would be expected (24). The modulus is decreased and the elongation at break is increased. The effect is more pronounced for lower molecular weight

than for higher molecular weight samples. This is because the higher the molecular weight the greater the frequency of ordered regions in the randomly coiled polymer matrix. Hence the higher the intermolecular attraction and the less sensitive the polymer is to plasticization with a given amount of plasticizer. This is evident from Fig. 3.11.

3.6.2 Branching

The elastic properties of the polymer, the yield stress and the elastic modulus, increases with branching upto a limit beyond which further branching decreases these properties, Figs. 3.9a and 3.9b. Like the adhesion, Fig. 3.5, the rise is sharper for polymer samples prepared at 40°C than for those prepared at 70°C. As was observed in Section 3.3 there is a stricking resemblance between the variation of the elastic properties of the polymer films, and the variation of adhesion, with branching. The pattern of Fig. 3.5 was explained in Section 3.2 in terms of changes in the viscosity of the polymer solution and the configuration of the polymer chain molecules. The pattern of Figs. 3.9a and 3.9b may be explained from the point of view of the factors affecting the elasticity of polymeric materials. It may be relevant too to mention here that the yield stress is a measure of the elasticity of the polymer (49, 50).

The necessary and sufficient conditions for long-range elasticity of a material is the presence of long chains and the possession of sufficient internal mobility by the system. Long chains, as in polymers,

allow the accomodation of large deformations merely through rearrangement of the configuration of the chains, and internal mobility allows the required rearrangements of chain configuration during deformation and during recovery as well (40).

Polyvinyl acetate satisfies the first requirement of long chains, which, in itself, is a characteristic of all polymers. The relatively shorter chains of samples prepared at 70°C permit higher mobility of these chains (50). It is not surprising, therefore, that before the onset of excessive branching, that is at low conversions, the samples prepared at 70°C have much higher values of modulus and yield stress than their counterparts prepared at 40°C.

There is very small rise in both yield stress and modulus with increasing conversion at 70°C and below 60% conversion. This could be due to the little change in the configuration of the polymer chains produced at this temperature (41). Within the same region and upto about 75% conversion a sharp rise in both the yield stress and the modulus is observed for samples prepared at 40°C due to the comparatively greater number of chain segments being added to the backbone chain with conversion at this temperature compared to what obtains at 70°C (41).

The fall in the elastic properties after some percentage conversion could be due to the coiling of the polymer chains discussed in Sections 3.1 and 3.2. Such chain coiling decreases the ability of the polymer chains to align themselves in the direction of the applied stress during deformation, thus decreasing the elasticity of the polymer. The

effect is more pronounced for samples prepared at 70°C because coiled short chains are less likely to have long-range ordered regions.

The effect of branching on the ultimate tensile strength and the percent elongation at break is not clear from the results shown in Fig. 3.6.1. The factors controlling both the tenacity (ultimate tensile strength), and the elongation at break of the polymer are its ability to form crystallites at the rubbery flow region when it is stretched beyond the elastic limit, and the mobility of the chains respectively (40). The ability of the polymer chains to form crystallites depends on the ease with which the chain segments can form ordered patterns. Obviously this ease should decrease with branching, but the decrease would depend not only on the type and nature of branching but also on the behaviour of the polymer chains in the solution from which the films are cast. It is not surprising then that no order was observed for tenacity as branching increases. Similarly no order was observed for elongation at break since although branching would reduce internal friction between chains, due to increase in the number of chain ends (50), and therefore increase elongation, the load at which rapture occurs would depend on the extent to which the chain segments are able to form crystallites.

3.6.3 Molecular weight

Upto about 10-15% plasticizer content, Tables 3.6.2 and 3.6.3, and Figs. 3.10 and 3.11 show that as the molecular weight of the polymer increases the modulus decreases. This was explained and backed with

literature support in Section 3.3.

Tenacity increases with molecular weight in contrast to the trends of modulus and yield stress. Tenacity has been explained to depend on the extent to which the chains can form crystallites while flowing in the rubbery region as they are stretched beyond the elastic limit of the material by the applied stress. Higher molecular weight analogs have greater ability to form such crystallites by virtue of their longer chains. Since the longer the chain the greater the probability of finding ordered regions along the length. Formation of the crystallites leads to toughness and embrittlement of the polymer (50), this requires the application of greater stress to further deform and subsequently rupture the polymeric material. The greater the ability of the polymer to form crystallites, therefore, the greater the stress needed to rupture the polymeric material, so that tenacity increases with molecular weight (40).

Upto about 10% plasticizer content, elongation at break seems to decrease with decreasing molecular weight, but the trend is again not uniform as was observed with the more highly branched samples. The explanations rendered in Section 3.6.2 may, therefore, be applicable here too.

3.6.4 A summary of the dependence of adhesion on both the viscosity and the mechanical properties of polyvinyl acetate

To illustrate the striking similarity in the dependence of adhesion on both the viscostiy and the mechanical properties of the polymer, as adhesion varies with both branching and molecular weight, data from Tables 3.1.2, 3.2. and 3.6.1, and Tables 3.3.2, 3.3.3. and 3.6.3 respectively, have been summarised in Tables 3.6.4 and 3.6.5.

It is conclusive from these last two Tables that adhesive strength is as dependent on the viscosity of the polymer solutions, from which the adhesive is applied, as on the mechanical properties of the dried polymer films.

CONCLUSIONS

The following conclusions may made from the various results of this study:

1. If polyvinyl acetate is to be the major component of an adhesive formulation, the polymer should be synthesized to obtain molecular weights ($\bar{M}_v$) in the region of about 5×10^3 to 5×10^4 in order to obtain optimum performance of the adhesive. Lower molecular weight polymers will have very low elongation at break and higher molecular weight polymers will have low elastic modulus. Low elongation at break and low elastic modulus amount to poor mechanical properties of the adhesive film.

2. Branching, if moderate, improves the performance of polyvinyl acetate adhesives. It is therefore advisable to synthesize the polymer with some amount of side chains. Both the length of the chains and the number of side chains should be such as to permit the polymer chains to remain extended in solution or in the medium in which the adhesive is used.

3. To obtain the polymer possessing reasonable amount of branching and having molecular weight in the region stated above, it is advisable to allow conversion to attain a value between about 55% to 75%, especially in equeous phase polymerizations in the absence of chain transfer agents. The temperature of polymerization, should be maintained between 50° and 60°C whichever technique is used for polymerization.

3. The wet tack of the adhesive in aqueous suspensions is poor. It is, therefore, advisable to isolate the polymer from the aqueous phase polymerization products. The most suitable solvent for dissolving the isolated and purified polymer should be a solvent that will dissolve sufficient quantity of the polymer without appreciable increase in the viscosity. It should also be volatile in order to evaporate easily from the applied adhesive providing for quick tack. Toluene, benzene, chloroform, or acetone are much more recommendable in this regard than alcohols or some other solvents.

4. If plasticized with dibutyl phthalate, about 10% of the plasticizer seems to give optimum adhesion. The suitability of some other plasticizers was not investigated.

5. Heat treatment of the adhesive joint, where this is possible, gives much better bond strength than the untreated joint. The optimum temperature of heat treatment may depend on the molecular weight of the polymer. A temperature as high as 160°C has been found to be suitable for an average molecular weight of 2×10^5 in this study. A higher temperature may still give better result but this was not investigated.

6. The adhesion of the polymer to wood, glass, and metal was found to be excellent. In most tests using an Instron machine, and in particular for bonding to wood and glass, the substrates yielded before the thin film of adhesive forming the bond.

7. Although reports exist to the effect that the heat and water sensitivity of the polymer may be improved by increasing the molecular

weight and introducing cross linkages into the polymer chains (24), the results here show that very high molecular weights and excessive crosslinking could greatly reduce the adhesiveness of the polymer. Therefore a much better means of reducing the heat and water sensitively of the polymer would be incorporation of groups that are less water sensitive than polyvinyl acetate to the backbone chain either by phsyical blending or by co-polymerization. Such a group should also have good adhesive properties and ethylene, acrylics, or styrene may be very recommendable in this regard (24).

8. The author is of the opinion that the most economic way to produce polyvinyl acetate with good adhesive properties seems to be by solution polymerization in a solvent having a fairly high chain transfer constant for the polymer. The polymer from such system needs not be isolated and could be plasticized and used directly. Recommendable solvents, therefore, would include benzene, chloroform, toluene or acetone depending on the relative costs and the ease of handling.

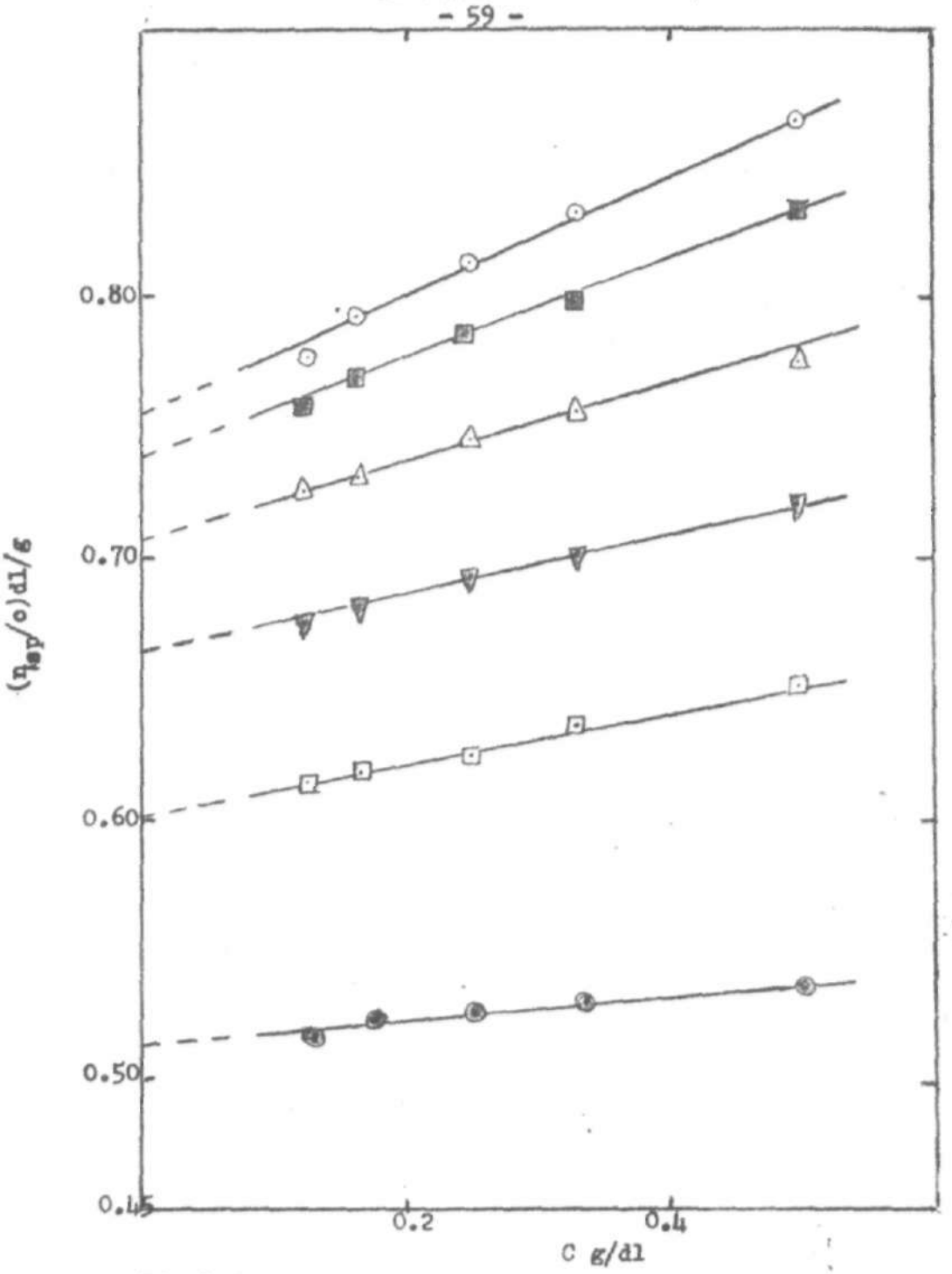


Fig.3.1a

Graphs of reduced viscosity (η_{sp}/c) against concentration (C) for unfractionated samples of PVAc. prepared at 40°C for different lengths of time:

⊙, 0.5 hrs.; ■, 1 hr.; △, 2 hrs.; ▼ 4 hrs.

⊡, 8 hrs. ● 22 hrs.

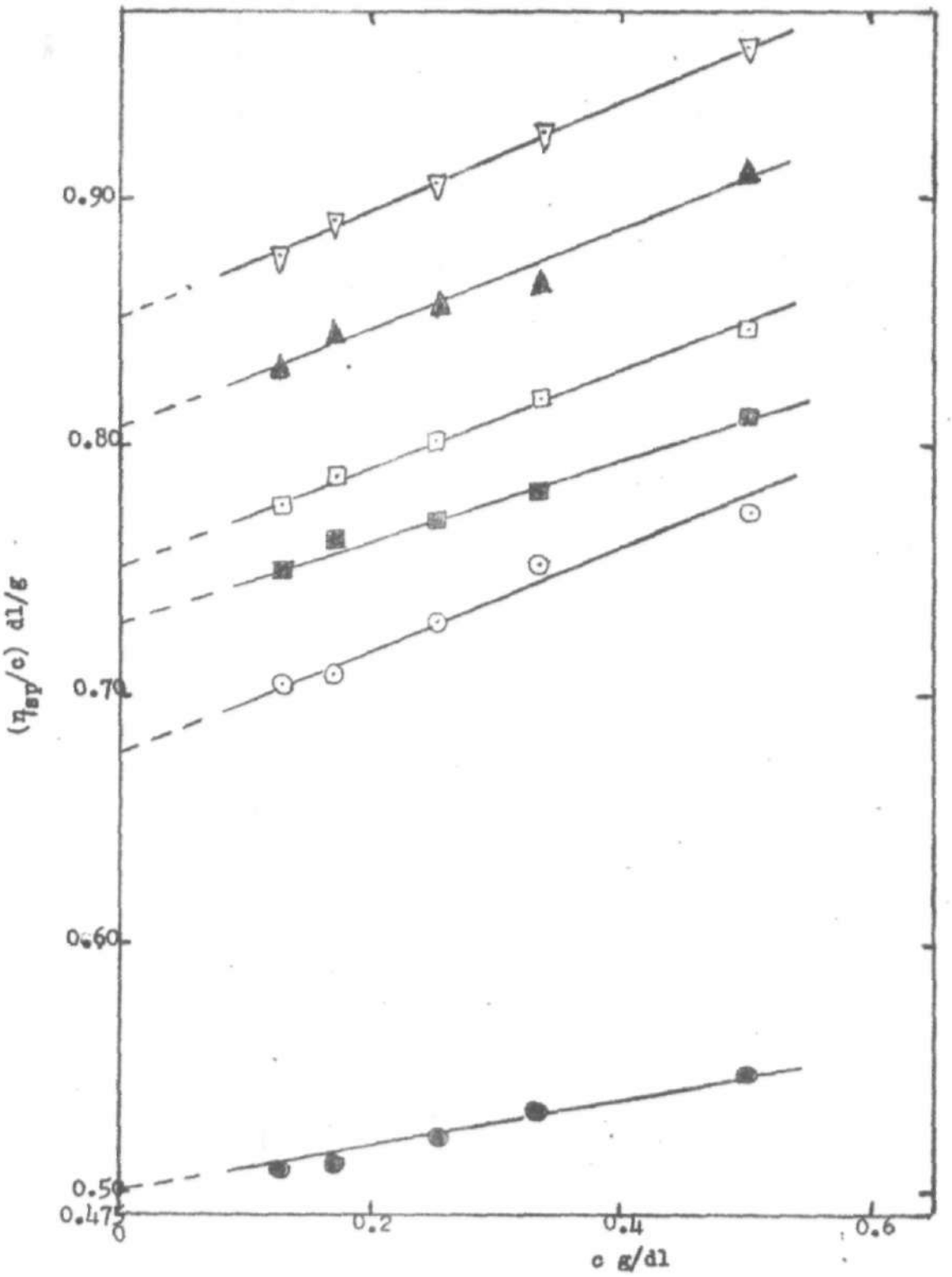


Fig. 3.1b

Graphs of reduced viscosity (η_{sp}/c) against concentration (c) for unfractionated samples of PVAc. prepared at 70°C for different lengths of time:

⊙, 5 mins.; ⊡, 10 mins.; ◭, 15 mins.;
▽, 1 hr. ; ■, 8 hrs. ; ●, 22 hrs.

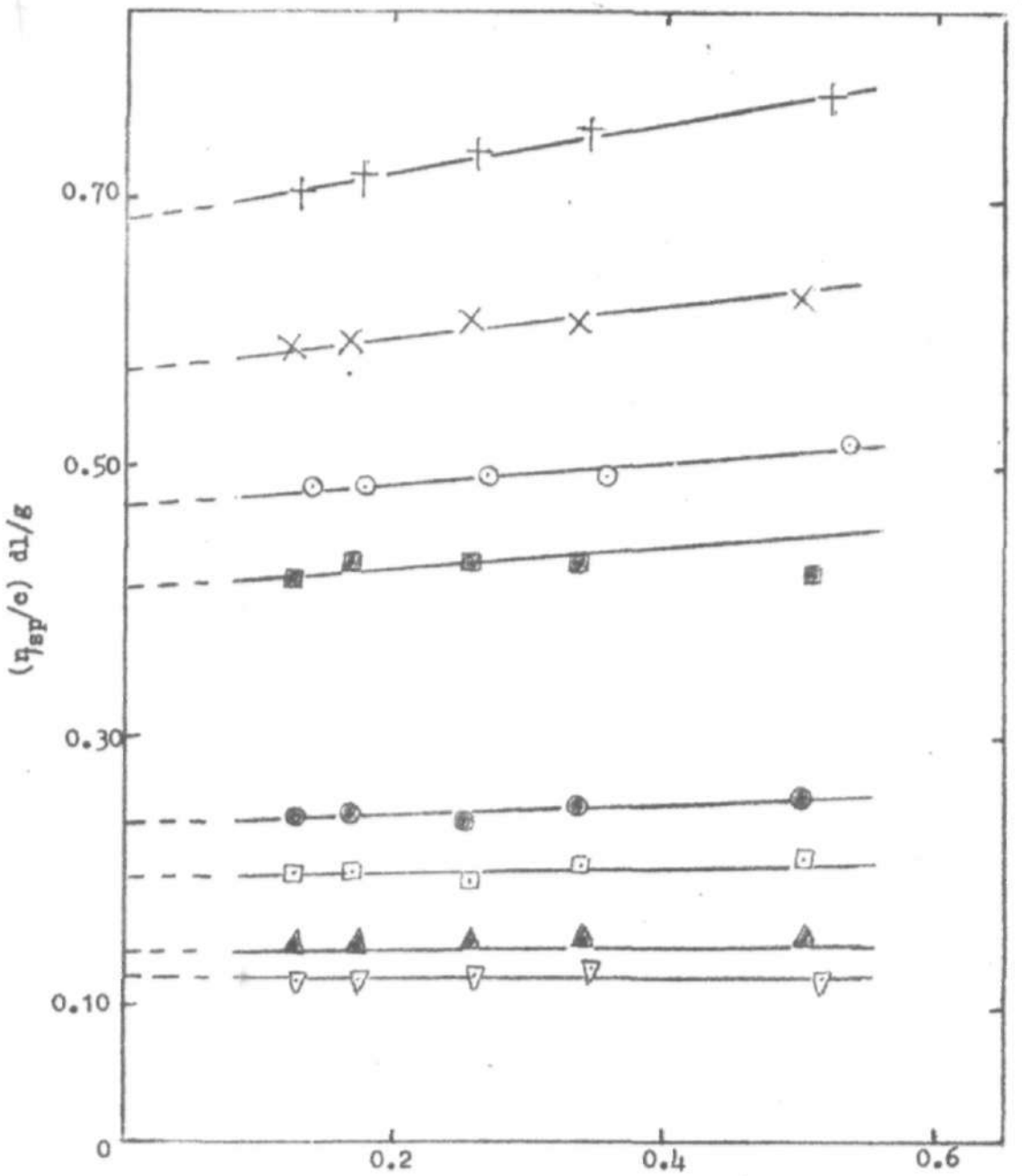


Fig.3.2

Graphs of reduced Viscosity (η_{sp}/c) against concentration (C) for unfractionated samples of PVAc. prepared under different conditions to vary the molecular weight:

B_2; B_0; B_ϕ; B_3; B_4; B_5; B_6; B_7.

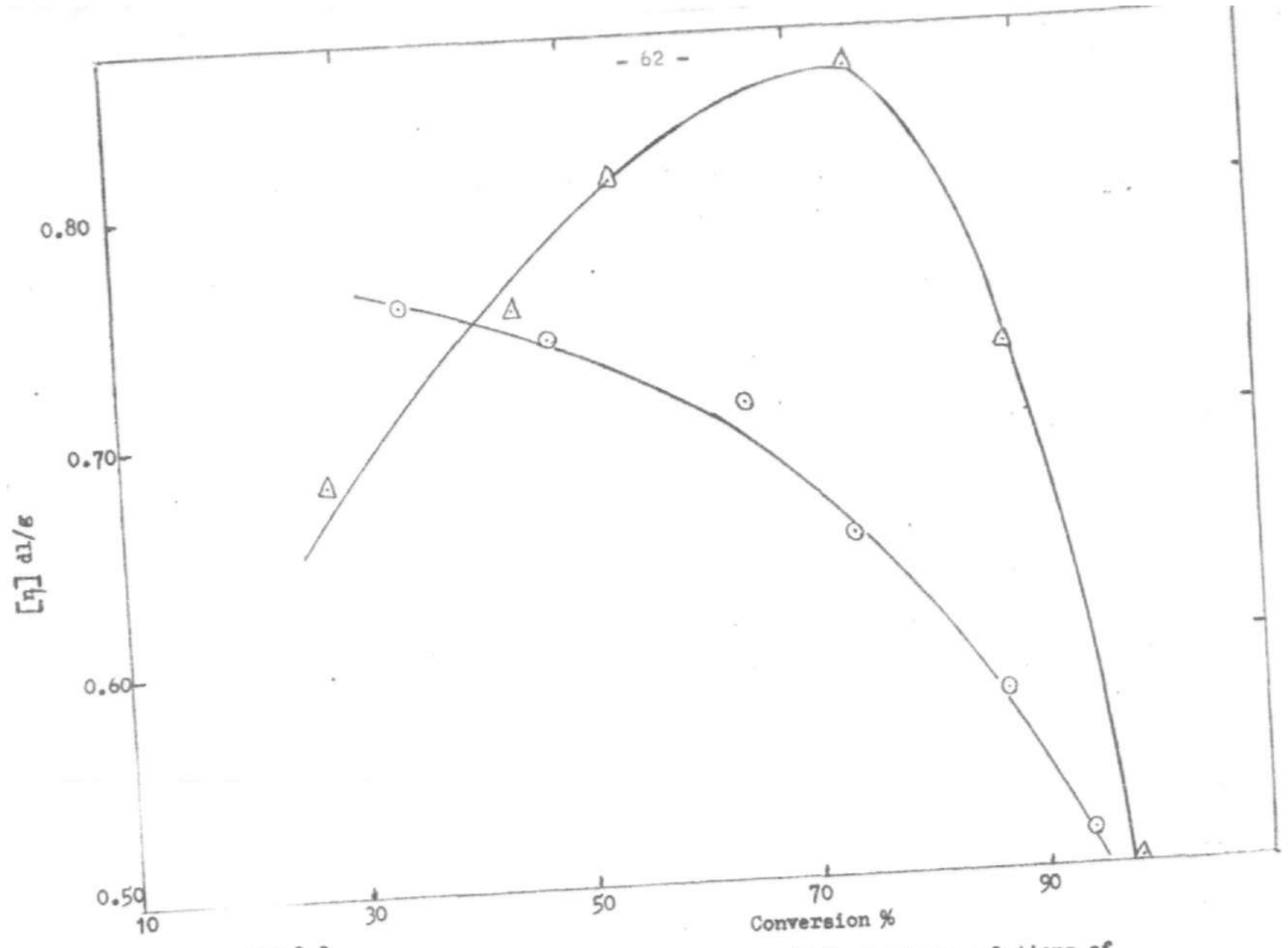


Fig.3.3

Variation of the limiting viscosity, [η] of dilute solutions of unfractionated PVAc with conversion at different temps. -⊙-, 40°C; -△-, 70°C.

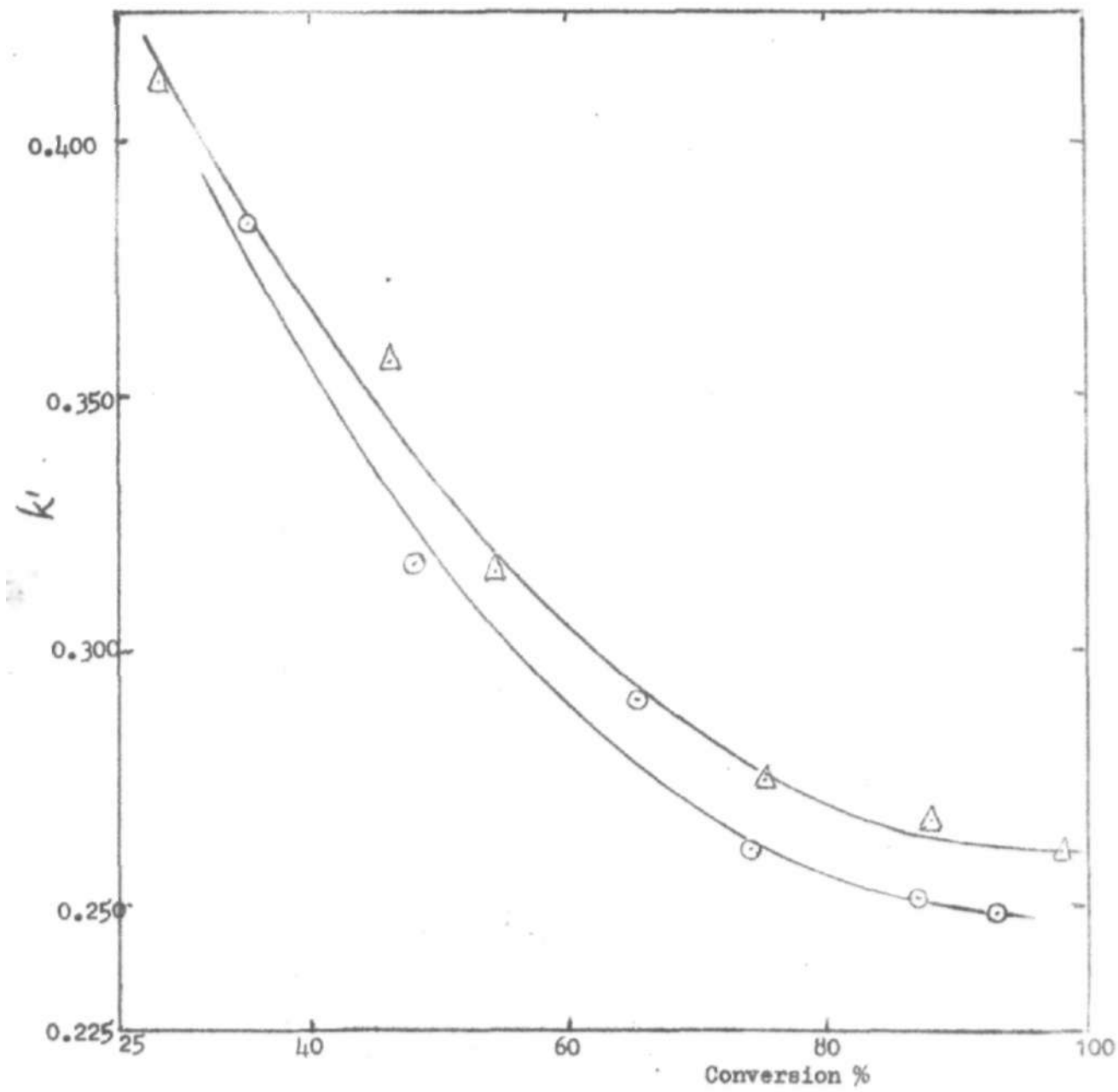


Fig.3.4

Variation of the Huggins' constant, k', of dilute solutions of unfractionated PVAc with conversion at different temps. ⊙, 40°C; Δ, 70°C.

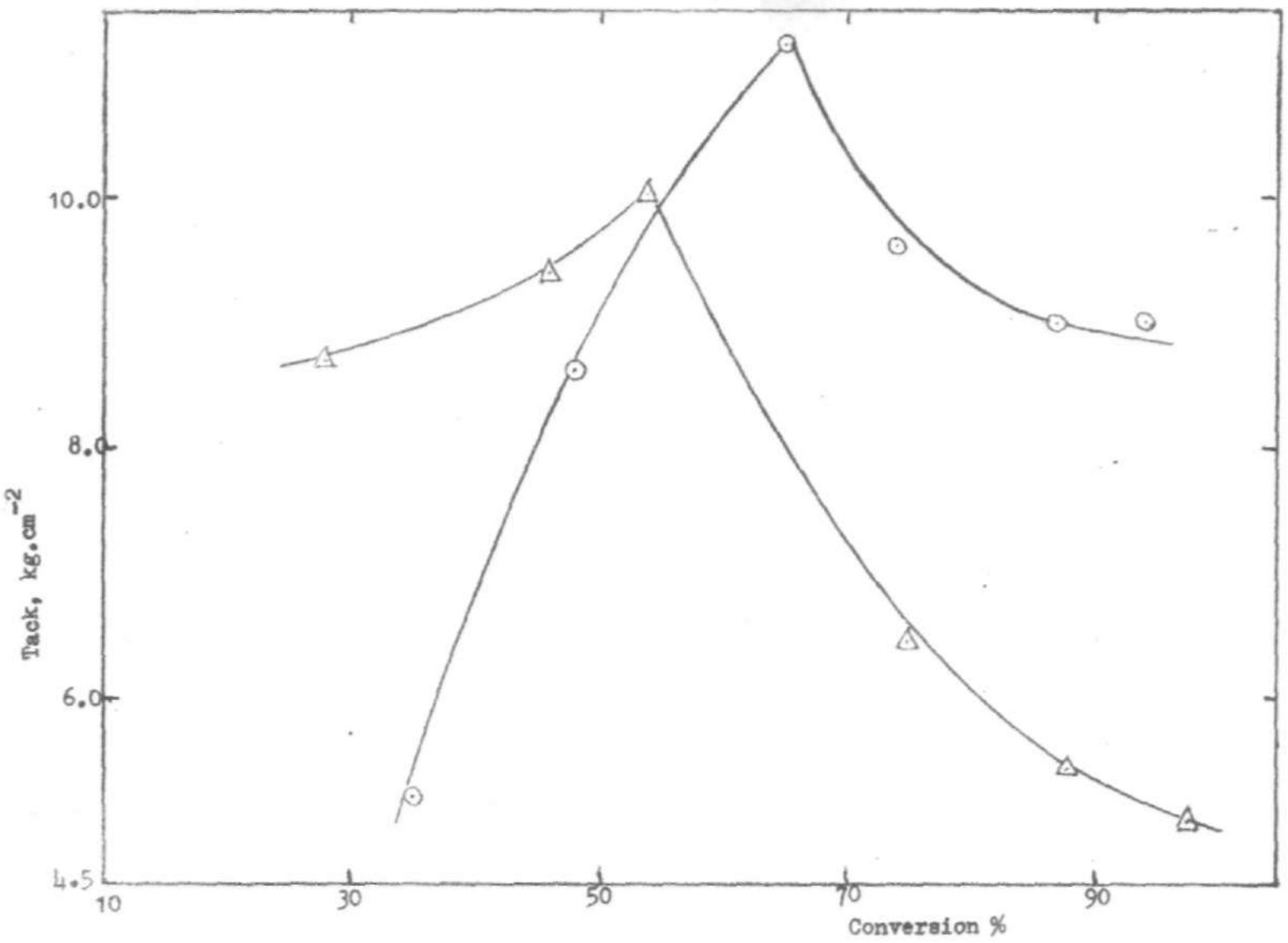


Fig.3.5

Dependence of the adhesion of PVAc on the extent of conversion at different temps. -⊙-, 40°C; -△-, 70°C.

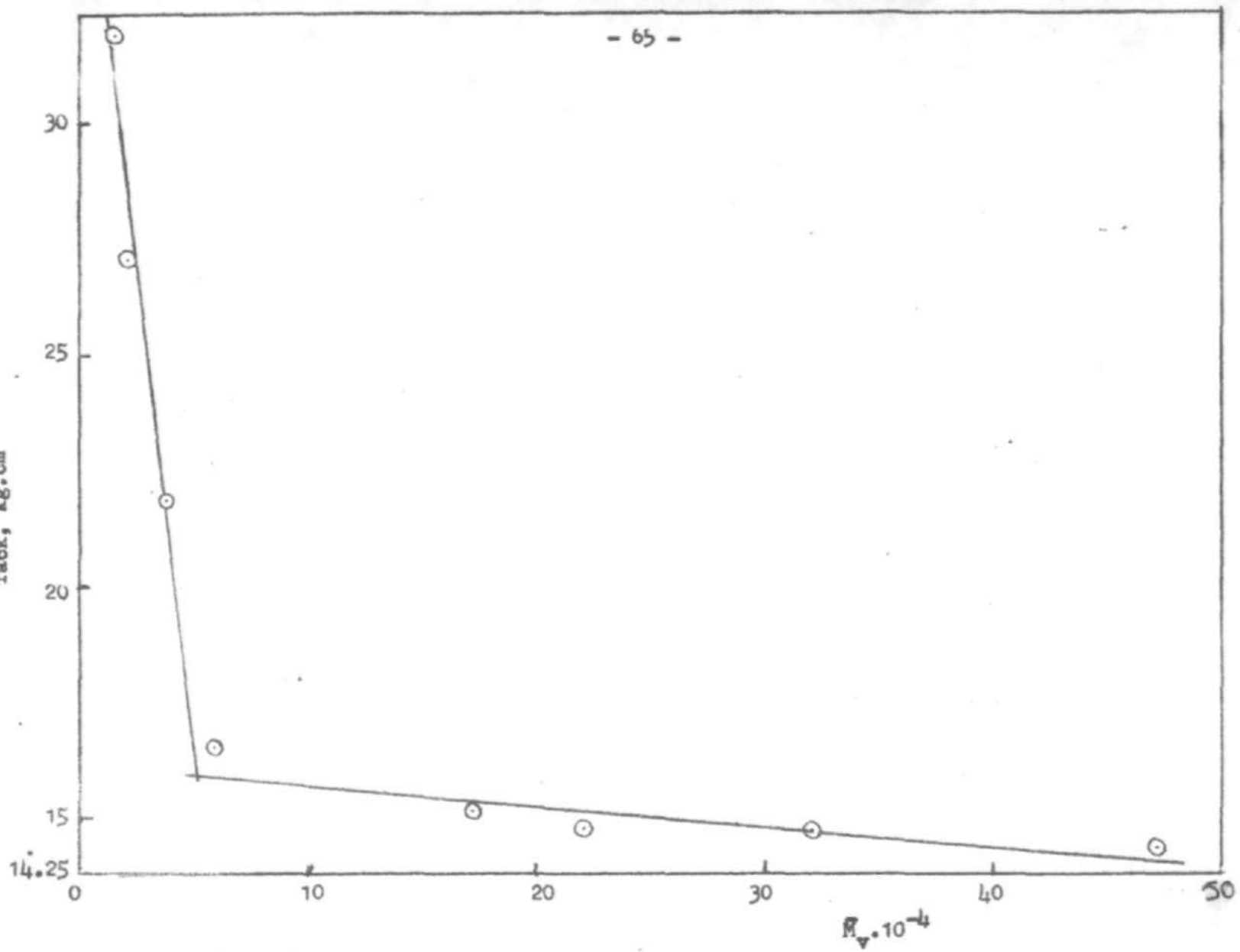


Fig.3.6

Dependence of the adhesion of PVAc on the molecular weight

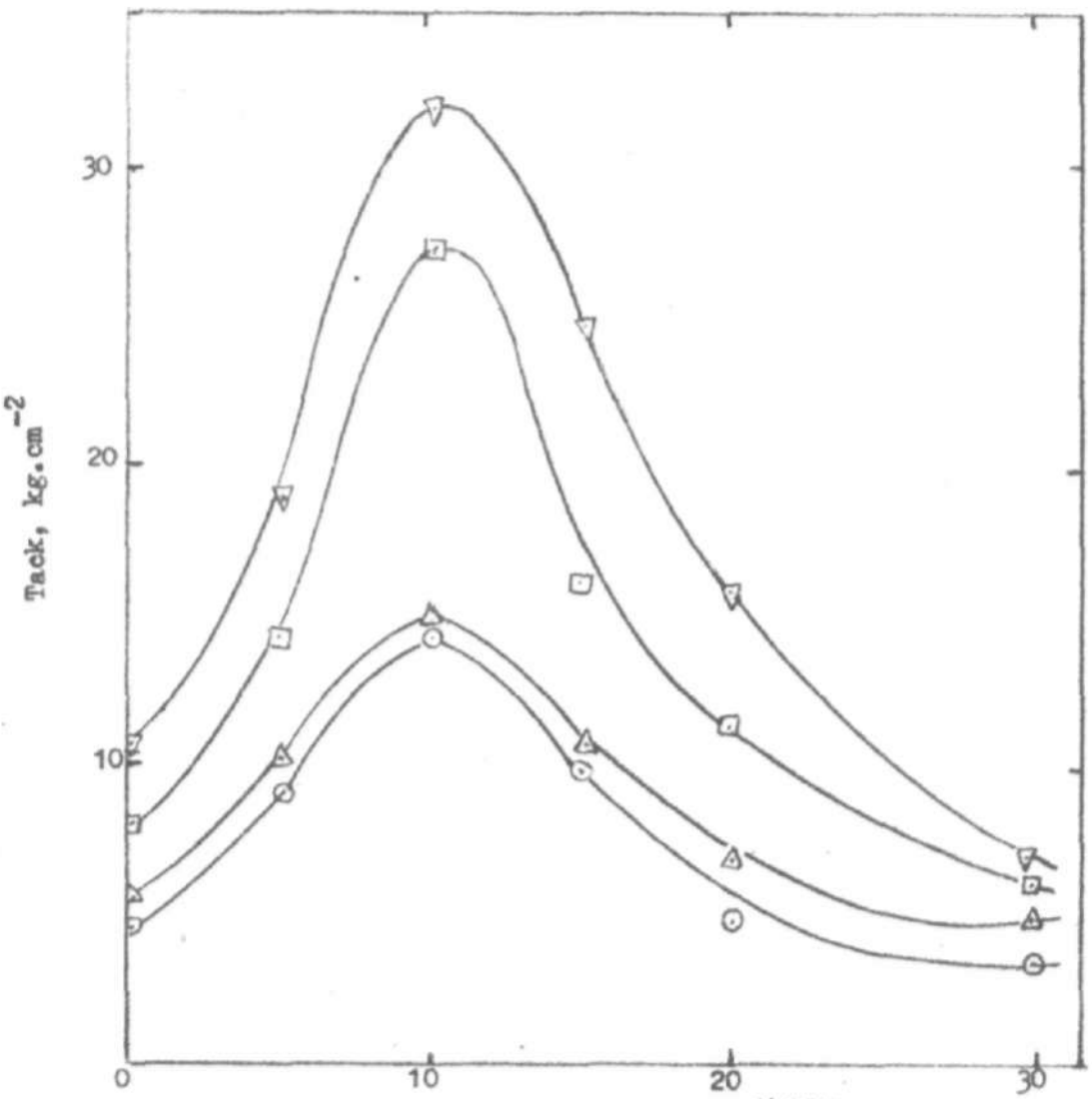


Fig.3.7

Variation of the adhesion of PVAc with the percent plasticization (using dibutyl phthalate, DBP)

$-\bigcirc-$ B_2; $-\triangle-$ B_1; $-\square-$ B_6; $-\triangledown-$ B_7.

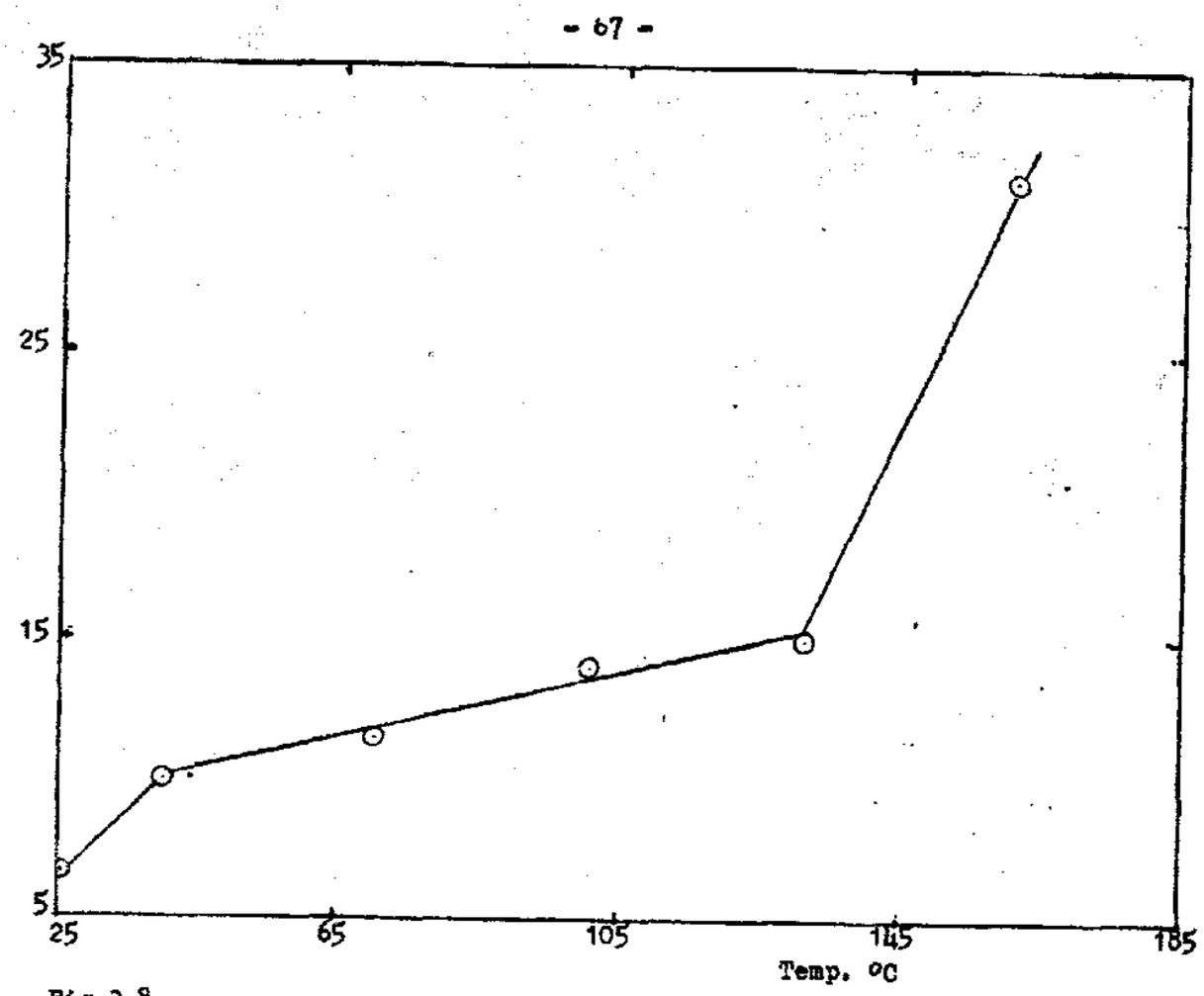


Fig.3.8

Variations in the adhesive strength of PVAc adhints when heat-set at various temperatures for 3 hrs.

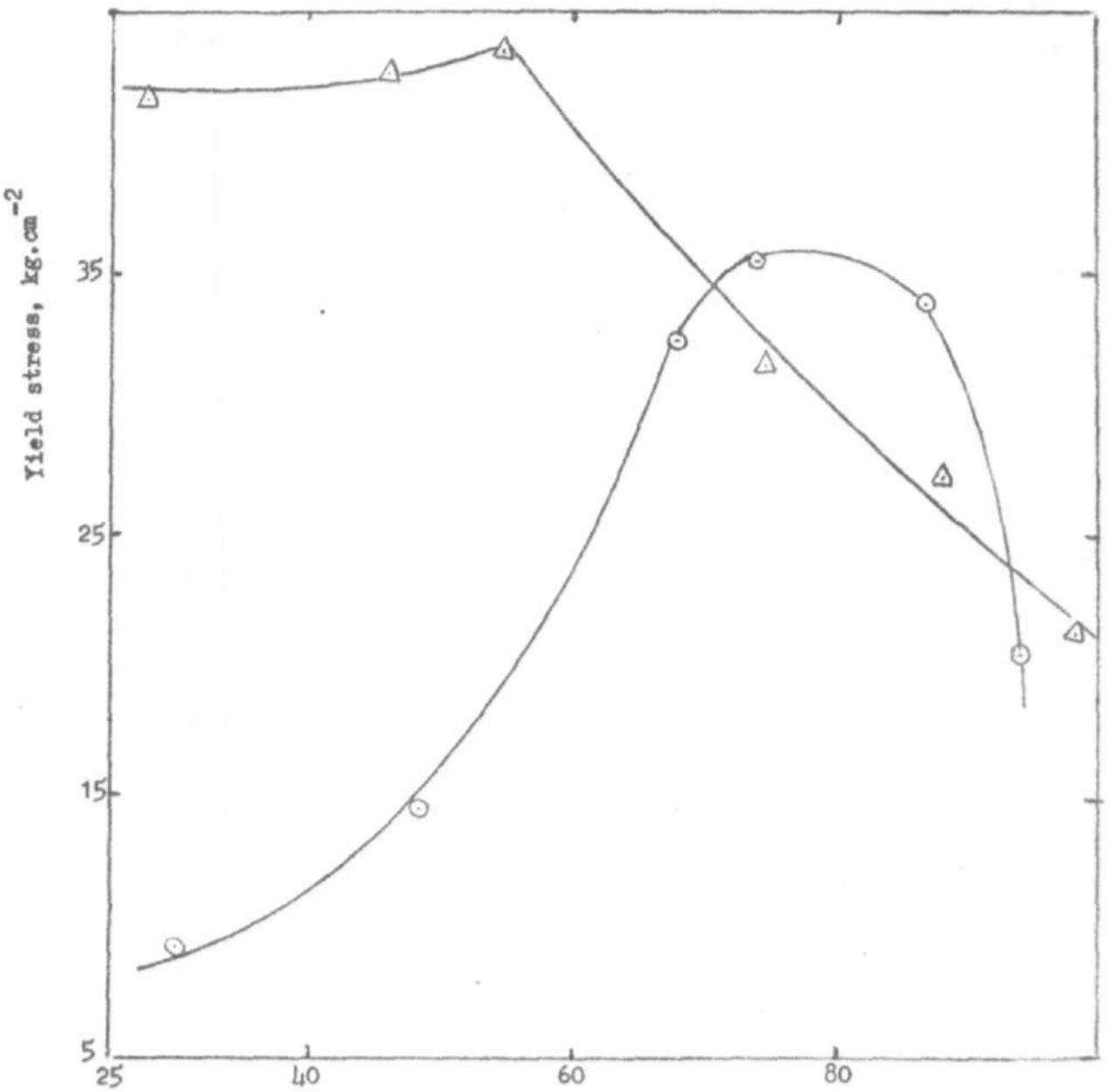


Fig.3.9a

Variation of the elasticity (yield stress) of films of PVAc prepared to different conversions at different temps.

$40^{\circ}C$; -⊙-, $40^{\circ}C$; -△-, $70^{\circ}C$

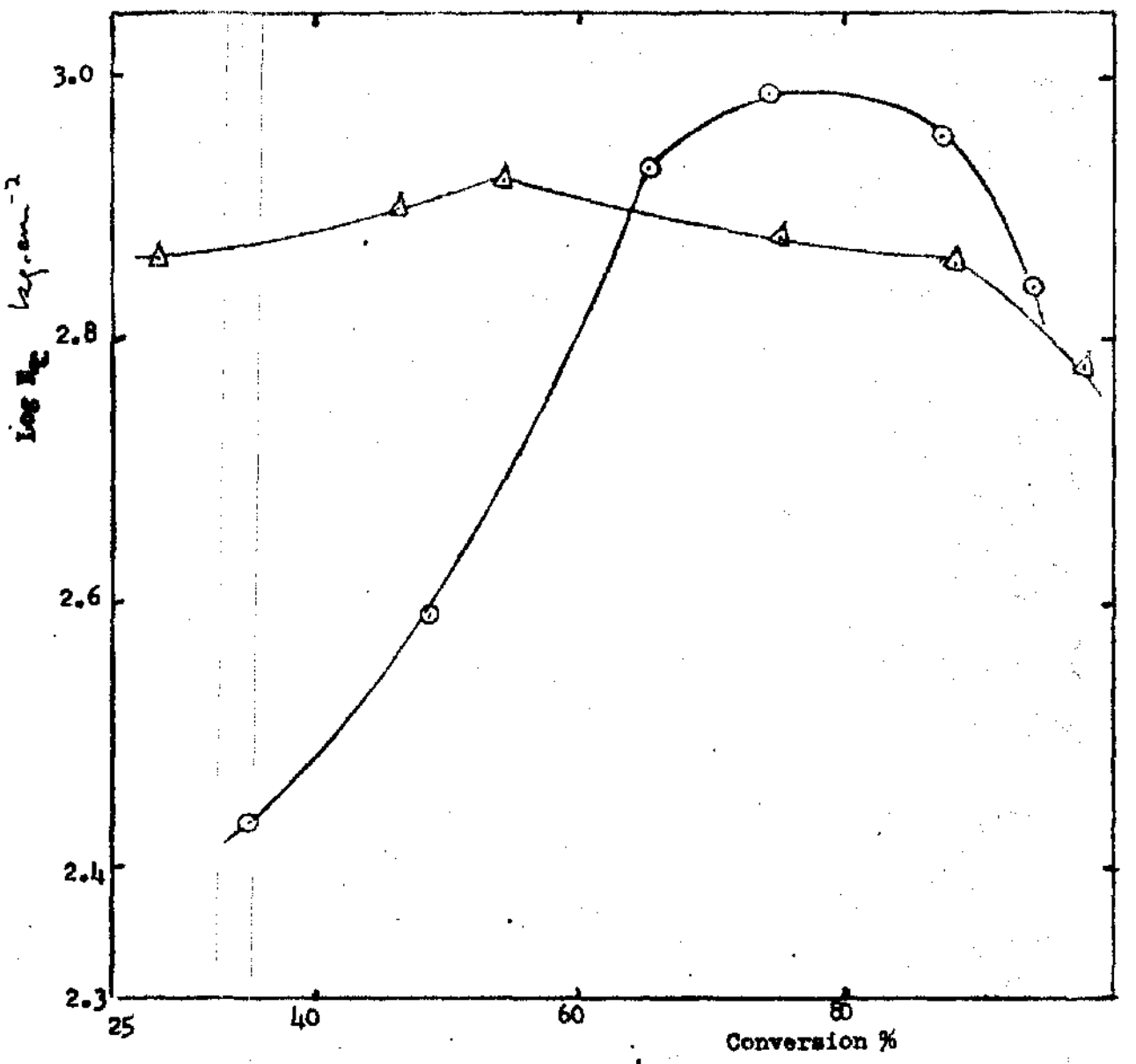


Fig.3.9b

Variation of the modulus (E_t) of films of PVAc prepared to different conversions at different temps.

-○-, 40°C.; -△-, 70°C

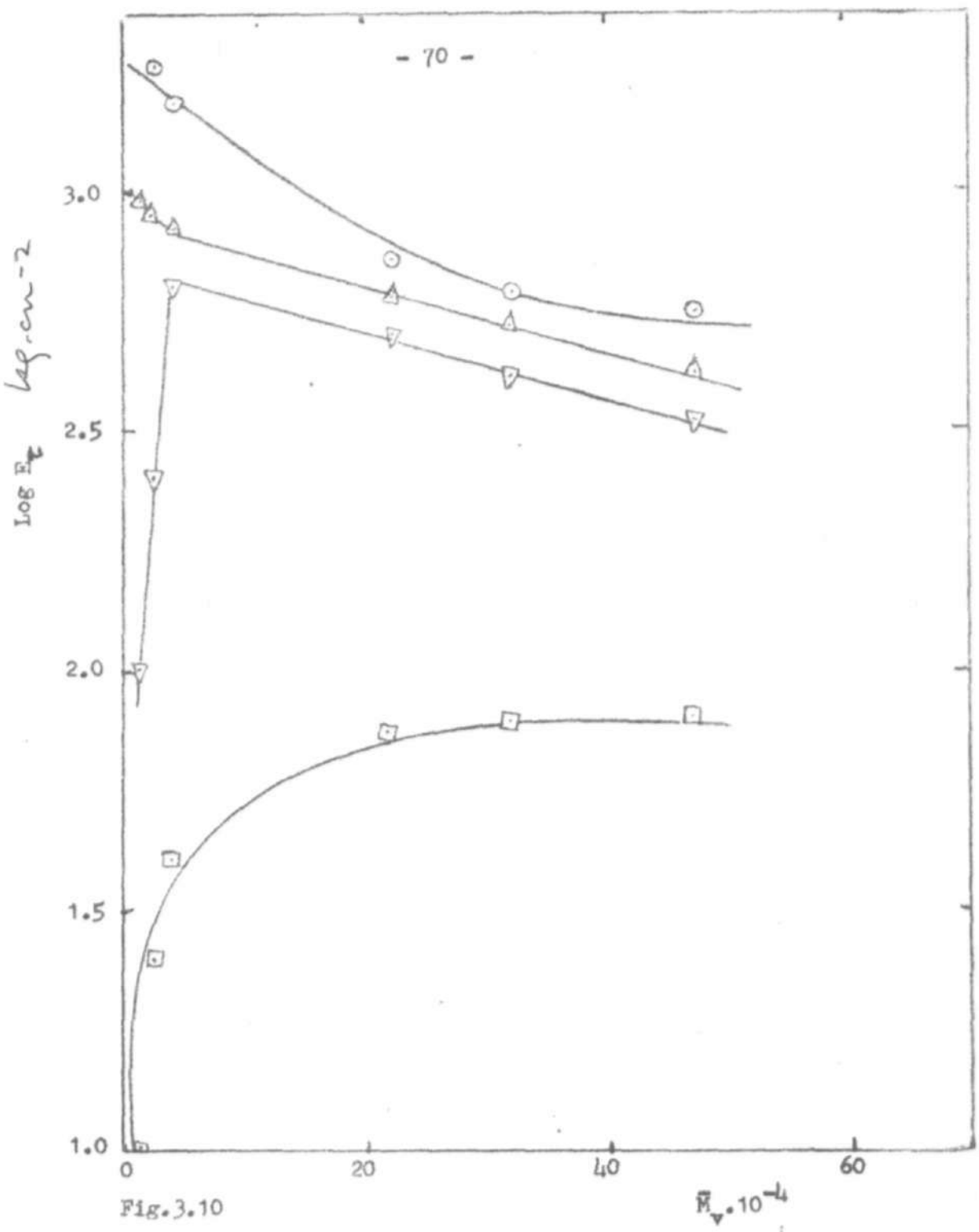


Fig.3.10

Effect of plasticization with DBP on the tensile modulus of films of PVAc having different molecular weights

—○—, 5%; —△—, 10%; —▽—, 15%; —□—, 20%.

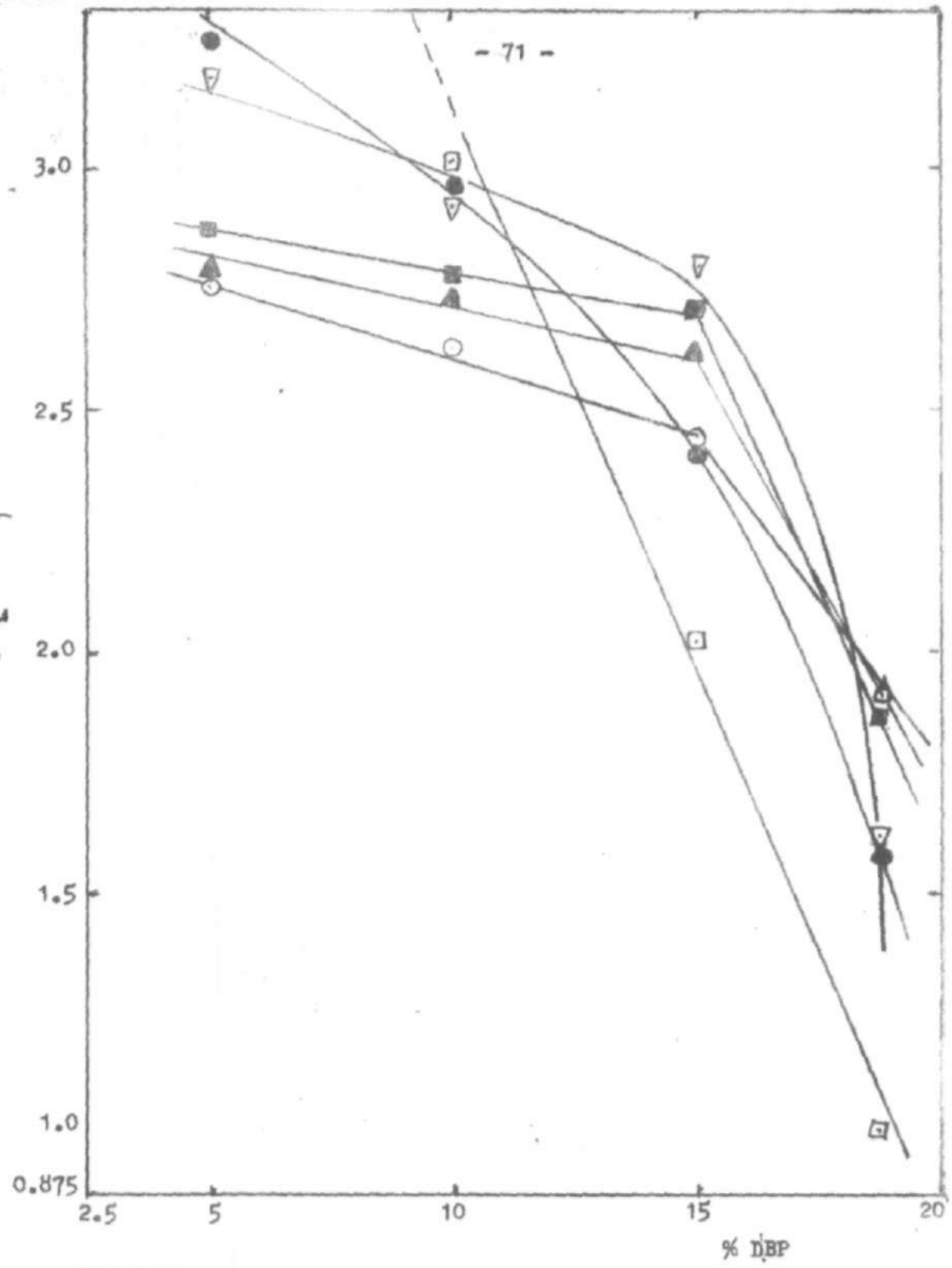


Fig.3.11

Dependence of the tensile modulus of films of PVAc having different molecular weights on the percent plasticization.

-⊙-, B_2; -▲-, B_0; -▣-, B_1; -▽-, B_5; -●-, B_6; -⊡-, B_7.

Table 3.0

Adhesion of polyvinyl acetate adhesives, prepared from the emulsion and solution, to wood, glass, aluminium, and zinc strips.

Substrate	Emulsion, tack, $kg.cm^{-2}$	Solution tack, $kg.cm^{-2}$
Wood	11.8	24.0
glass	5.8	11.2 (glass yielded)
aluminium	6.3	18.8
zinc	7.1	20.5

Table 3.1.1

Conditions and recipes for the preparation of samples of PVAc of different converions.

Sample	Temp. °C	Time hrs : mins	$\frac{[Na_2S_2O_8]}{[VAc]}$ % (w/w)	[VAc] $m.l^{-1}$	Conversion %
A_1	40	30	1.75	4.302	35
A_2	40	1	1.75	4.302	48
A_3	40	2	1.75	4.302	65
A_4	40	4	1.75	4.302	74
A_5	40	8	1.75	4.302	87
A_6	40	22	1.75	4.302	94
A_7	70	5	0.325	4.302	28
A_8	70	10	0.325	4.302	46
A_9	70	15	0.325	4.302	54
A_{10}	70	1	0.325	4.302	75
A_{11}	70	4	0.325	4.302	88
A_{12}	70	22	0.325	4.302	98

Table 3.1.2

Results of the measurement of solution viscosities of unfractionated PVAc. prepared to different conversions

Sample	A_1	A_2	A_3	A_4	A_5	A_6	A_7	A_8	A_9	A_{10}	A_{11}	A_{12}
Conversion %	35	48	65	74	84	94	28	46	54	75	88	98
$[\eta]$ dl/g	0.757	0,740	0.709	0.650	0.602	0.515	0.680	0.752	0.809	0.855	0.730	0.500
k^1	0.384	0.329	0.290	0.260	0.251	0.248	0.368	0.357	0.315	0.274	0.267	0.200

Table 3.2

Effect of conversion on the adhesion of PVAc.

Sample	A_1	A_2	A_3	A_4	A_5	A_6	A_7	A_8	A_9	A_{10}	A_{11}	A_{12}
Conversion %	35	48	65	74	84	94	28	46	54	75	88	98
Tack $k_g.cm^{-2}$	5.2	8.6	11.2	9.6	9.0	9.0	8.7	9.0	10.0	6.9	5.4	5.0

Table 3.3.1

Conditions and recipes for the preparation of PVAc. of different molecular weights.

Sample	Temp. °C	Time hrs.	AIBN / VAc % w/w	R / AIBN % w/w x 10^2	VAc / MeOH % v/v	Yield %
B_1	65	0.5	2.0	-	-	56
B_2	60	1	1.0	-	-	34
B_5	60	4	0.9	-	40/50	41
B_6	60	7.5	1.0	-	40/60	36
B_7	60	14.5	1.5	-	25/75	57
B_0	55	2	0.7	-	-	38
B_3	55	5	1.0	1.67	-	47
B_4	50	24	1.0	3.34	-	61

R = nitrobenzene

Table 3.3.2

Results of the measurement of solution viscosities of unfractionated PVAc different molecular weights.

Samples	k'	$[\eta]$	$\bar{M}_v \cdot 10^{-4}$
B_2	0.370	0.690	47
B_0	0.371	0.575	32
B_1	0.368	0.475	22
B_3	0.412	0.415	17
B_4	0.451	0.240	5.7
B_5	0.374	0.200	3.9
B_6	0.381	0.145	2.1
B_7	0.392	0.125	1.5

Table 3.3.3

Results of adhesion tests on samples of PVAc of different molecular weights.

Sample	B_2	B_0	B_1	B_3	B_4	B_5	B_6	B_7
Md.wt. $\bar{M}v.10^{-4}$	47	32	22	17	5.7	3.9	2.1	1.5
Tack $k_g.cm^{-2}$	14.4	14.8	14.8	15.2	16.6	22.0	27.2	32.0

Table 3.4

Results of adhesion tests on some samples of PVAc plasticized with dibutyl phthalate (DBP).

Sample	% DBP					
	0	5	10	15	20	30
	Tack in $k_g.cm^2$					
B_2	4.6	9.2	14.4	10.0	4.9	3.5
B_1	5.5	10.0	14.8	10.8	7.0	5.1
B_6	8.0	14.0	27.2	16.0	11.2	5.9
B_7	10.5	18.8	32.0	24.4	15.6	6.8

Table 3.5

Results of adhesion tests on a sample of PVAc. heat set at different temperatures for 3 hours.

Heat getting temp, ^oC	25	40	70	100	130	160
Tack $k_g.cm^{-2}$	6.6	9.9	11.2	13.9	14.6	31.1

Table 3.6.1

Results of mechanical tests on films of PVAc. prepared to different conversions and plasticized with 10% DBP.

Sample	Tensile modulus E_t kg.cm^{-2}	Yield stress kg.cm^{-2}	Ultimate tensile stress kg.cm^{-2}	Elongation at break %
A_1	268	9.3	55.7	352
A_2	391	14.7	57.1	320
A_3	851	32.5	95.4	340
A_4	977	35.6	93.8	360
A_5	917	34.0	90.7	360
A_6	694	20.7	74.1	336
A_7	735	41.7	141.2	420
A_8	789	42.6	93.7	340
A_9	833	48.7	136.0	432
A_{10}	754	49.6	89.5	310
A_{11}	724	27.3	83.7	368
A_{12}	602	21.3	112.0	342

Table 3.6.2

Effect of plasticiation with dibutyl phthalate, DBP, on some mechanical properties of PVAc having different molecular weights.

Sample	Mol.wt. $\bar{M}_v \cdot 10^{-4}$	% DBP 0		5		10		15		20	
		E_t	b	E_t	b	E_t	b	E_t	b	E_t	b
B_2	47	High >1000	low 1<	568	400	423	400	335	444	83	528
B_0	32	>1000	1<	612	301	543	372	421	489	81	549
B_1	22	>1000	1<	760	240	602	280	516	460	78	578
B_5	3.9	Very high >10,000	1<	1528	296	854	312	632	548	42	916
B_6	2.1	>10,000	1<	1833	292	916	361	258	764	38	852
B_7	1.5	>10,000	1<	very high	low 1<	1031	40	122	1600	10	very high

E_t = tensile modulus in $kg.cm^{-2}$

b = elongation at break in %

Table 3.6.3

Results of mechanical tests on films of PVAc having different molecular weights and plasticized with 10% DBP.

Sample	Mol.wt $\bar{M}_v \times 10^{-4}$	Elastic Modulus E_t kg.cm^{-2}	Ultimate Tensile Stress kg.cm^{-2}	Elongation at break %
B_2	47	423	150	400
B_0	32	543	128	372
B_1	22	602	91	280
B_3	17	654	89	300
B_4	5.7	712	81	366
B_5	3.9	854	81	362
B_6	2.1	916	76	361
B_7	1.5	1031	46	40

Table 3.6.4

A summary of the dependence of adhesion on both the viscosity of polymer solutions and the elastic modulus of polymer films for polyvinyl acetate prepared to different conversions.

Sample	Conversion %	Tack $kg.cm^{-2}$	Intrinsic viscosity $[\eta]$ dl/g	Elastic Modulus $E_t \times 10^{-2}$ $kg.cm^{-2}$
A_1	35	5.2	0.757	2.68
A_2	48	8.6	0.740	3.91
A_3	65	11.2	0.709	8.51
A_4	74	9.6	0.650	9.77
A_5	84	9.0	0.602	9.17
A_6	94	9.0	0.515	6.94
A_7	28	8.7	0.680	7.35
A_8	46	9.0	0.752	7.89
A_9	54	10.0	0.809	8.33
A_{10}	75	6.9	0.855	7.54
A_{11}	88	5.4	0.730	7.24
A_{12}	98	5.0	0.500	6.02

Table 3.6.5

A summary of the dependence of adhesion on both the viscosity of the polymer solution and the elastic modulus of the polymer film for samples of polyvinyl acetate having different molecular weight

Sample	Mol.wt. $\bar{M}_v \times 10^{-4}$	Tack $kg.cm^{-2}$	Intrinsic viscosity $[\eta]$ dl/g	Elastic Modulus $E_t \times 10^{-2}$ $kg.cm^{-2}$
B_2	47	14.4	0.690	4.23
B_0	32	14.8	0.575	5.43
B_1	22	14.8	0.475	6.02
B_3	17	15.2	0.415	6.54
B_4	5.7	16.6	0.240	7.12
B_5	3.9	22.0	0.200	8.54
B_6	2.1	27.2	0.145	9.16
B_7	1.5	32.0	0.125	10.31

APPENDIX A

Some Observations On the Preparation of Polyvinyl acetate using potassium persulphate

The behaviour of potassium persulphate and sodium dodecyl sulphate in suspension and emulsion polymerization of vinyl acetate.

Potassium persulphate is widely used as initiator in emulsion polymerizations in which sodium dodecyl (or lauryl) sulphate is used as the surfactant (6, 7, 9). The system was successfully used several times at the start of this work.

However, several attempts to repeat the work a few months after the first series of polymerizations proved very unsuccessful. Using the same amounts of reagents, 0.5_g $K_2S_2O_8$, and 0.5_g $C_{12}H_{25}OSO_3Na$ in 134^{cm^3} of water, it was observed that the surfactant separated from the system forming a rather attractive oily suspension each time the initiator was added. No polymerization was observed under such a situation even after a period of time that normally resulted in over 50% conversion.

Several attempts to vary the amount of initiator and/or surfactant were not successful, especially if the concentration of one reagent was kept constant and the other varied.

Only at extremely low concentrations of either was it possible to get a homogeneous system. For the surfactant this concentration was below the critical micelle concentration and for the initiator it was too low to permit polymerization at a reasonable rate at the

temperature of reaction.

In the absence of the initiator a comparatively large amount of surfactant could be dissolved and heated in the presence of sodium dihydrogen phosphate without separation. A little amount of potassium persulphate was, however, sufficient to cause precipitation.

In the absence of the initiator the separation was found to be a function of the pH of the medium, occuring both at very low pH (about 1) and at very high pH (about 13). On this basis the system was strongly buffered with much higher concentration of sodium dihydrogen phosphate than previously used but this did not help the situation. Indeed the use of potassium dihydrogen phosphate as buffer caused much quicker separation of the surfactant than previously was observed.

All reagents used were of high purity and reagents from different sources were tried, therefore, the effect could not be attributable to contamination.

On the basis of the observations above, a suggestion was made that the separation might be due to the comparatively lower solubilities of potassium salts than the sodium equivalents, hence the formation of potassium dodecyl sulphate when the ions of both $K_2S_2O_8$ and $C_{12}H_{25}OSO_3Na$ are in solution could lead to the precipitation of $C_{12}H_{25}OSO_3K$.

When NaH_2PO_4, $K_2S_2O_8$ and $C_{12}H_{25}OSO_3Na$ are all in solution, they ionize as follows:

$NaH_2PO_4 \rightleftharpoons Na^+ + H_2PO_4^-$ (1st ionization)

$C_{12}H_{25}OSO_3Na \rightleftharpoons Na^+ + C_{12}H_{25}OSO_3^-$

$K_2S_2O_8 \rightleftharpoons 2\,K^+ + 2SO_4^-$

Thus when equal amounts of the three reagents are dissolved (as was the usual practice in the work), there are equal chances (on the basis of concentration of ions only) for the formation of lauryl sodium or potassium/sulphate:

K^+ or $Na^+ + C_{12}H_{25}OSO_3^- \rightleftharpoons C_{12}H_{25}OSO_3$ K Na or

Formation of the potassium salt could lead to precipitation favouring the formation of more potassium salt. The precipitation of the surfactant will lead to the destabilisation of the monomer suspension and depending on the efficiency of the stirring or the interference of other factors, the rate of polymerization would be too slow to be convenient. These reasonings are in agreement with the increase in precipitation on prolonged standing and the slowed polymerization observed.

Apart from the concentrations of the salts other factors that could contribute to this phenomenom are the pH of the medium (see before) the ionic strength , and a lowering of the Kraft point (34).

Unfortunately the nature of this work did not permit a digression to study these factors in detail, hence no conclusive reason is given here for the separation of the surfactant on the addition of the

potassium salt.

However, on the basis of the above reasonings it was apparent that the use of sodium persulphate would not be likely to lead to the same behaviour. This was tried and found very successful. Sodium persulphate was, therefore, used for the rest of the study (Table 3.10). The stability of the suspension formed compares well with that formed using potassium persulphate. The reactions seemed slower but this could not be well established.

The author is of the view that the use of sodium persulphate should be preferable to the use of potassium persulphate to safeguard against similar occurence especially when the actual purity of the water being used is not certain.

Appendix B

Glossory of terms relating to, adhesives and mechanical testing (24)

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 STRENGTH The unit load applied in tension, compression, flexure, peel, impact, cleavage or shear, required to break adhesive assembly with failure accuring in or near the plane of the bond.

SET To convert an adhesive into a fixed or hardened state by chemical action or by physical action such as evaporation.

SUBSTRATE A material upon the surface of which an adhesive containing substance has been spread for any purpose

TACK The property of an adhesive that enables it to form a bond of measurable strength immediately after adhesive and adherend have been brought into contact under low pressure

ELONGATION The distance a film will stretch lengthwise before breaking expressed as a percentage

STRAIN A non-dimensional quantity, being a measure of the change, due to force, in the size or shape of a body referring to its original dimensions. It may be linear (tensile or compressive strain) or angular (shear strain)

STRESS The intensity at a point in a body of the internal forces or components of force, that act on a given plane through the point.

YIELD POINT The first stress in a material at which an increase in strain occurs without an increase in stress.

References

1) Schildknetch; C. E., "Vinyl and Related Polymers", John Wiley & Sons, Inc., N.Y. (1959).

2) Ham, G.E.; "Vinyl Polymerization", Part I, Edward Arnold (Publ.) Ltd., London (1967) pp 1-56, 207-290

3) Mayo, F.R.; J. Am. Chem. Soc., 65 (1943) 2324

4) Arnett, L.M.; & J.H. Peterson; J. Am. Chem. Soc., 74 (1952) 2031

5) Guha, T., et al.; J. Poly. Sci.; A-2 (1964) 1471

6) Dunn, A.S., & A.P. Tayler; Makromol. Chem. 83 (1965) 207

7) Napper, D.H. & A.G. Parts; J. Poly. Sci., 61 (1962) 113

8) Koltheff, I.M., & W.J. Dale; J. Am. Chem. Soc., 69 (1947) 441

9) French, D.M.; J. Poly. Sci., 32 (1958) 395

10) Konar, R.S., et al.; Ibid, A-2 (1964) 1481

11) Morton, M., & I. Piirma; Ibid, A-1 (1963) 3043

12) Standinger, H., & A. Schwalbac; Ann., 488 (1931) 8

13) Frankel, M., et al.; J. Chem. Soc., (1959) 3858

14) Kelly, D.J., J. Poly. Sci.; 59 (1962) S6

15) Wexler, H., & J. A. Mason; Ibid, A-3 (1965) 2903

16) Clarke, J.T., et al.; Makromol. Chem. 44/46 (1961) 427

17) Georgieff, R.K., et al.; J. Appl. Poly. Sci., 8 (1964) 889

18) Harkins, W.D.; J.Am. Chem. Soc. 69 (1947) 1428

19) Smith, W.V.; & R.H. Ewart; J. Chem. Phys. 16 (1948) 592

20) Howard, R.N.; J. Poly. Sci., 4 (1949) 273

21) Semenov, N.N.; Ibid 55 (1961) 563

22) Schulz, G.V.; Z. Elktrochem., 43 (1937) 479.

23) Huggins, M.L.; J. Am. Chem. Soc., 64 (1942) 277

24) Warson, H.; "The Applications of Synthetic Resin Emulsion", Ernst Benn Ltd., London (1972) pp. 22-23, 126-127, 147-164, 193-201, 279-300

25) Skeist, I. (editor); "Handbook of Adhesives", Reinhold Publ. Corp., Chapman & Hall Ltd., London (1975) pp 454-459

26) Voyutskii, S.S., & V. L. Vakyla; J. Appl. Poly. Sci., 7 (1963) 495

27) Zisman, W.A., Ind. & Eng. Chem. 88 (1963) 18

28) Alfrey, J., & M. Berdick; J. Poly. Sci., 3 (1948) 899

29) Sorenson, W.R., & T.W. Campbell, "Preparative Methods of Polymer Chemistry", 2nd ed. John Wiley & Sons Ltd., N.Y. (1968) p 239.

30) Melville, H.W., & P.R. Sewell; Makromol, Chem. 32 (1959) 139

31) Frielander, H.N., et al; J. Poly. Sci., A-1,4 (1966) 649

32) Pinner, S.H.; "A Practical Course in Polymer Chemistry", Pergamon Press, London (1961) p.53

33) Morikawa, T., & S. Miyao; CA47:5167 p

34) Weil, J.K., & F.D. Smith; J. Org. Chem., 27 (1962) 2950

35) Brandrup, J., & E.H. Immergut; (editors), "Polymer Handbook", 2nd ed., John Wiley & Sons Ltd., N.Y. (1975).

36) Harper, C.A.; (Editor-in-Chief) "Handbook of Plastics and Elastomers, McGraw-Hill Book Co., N.Y. (1975) pp 10-1-10-132

37) Melville, H.W., et. al; Makromol. Chem., 28 (1958) 140

38) Simha, R.J.; See ref. (37).

39) Gillespie T.; J. Poly. Sci., C-3 (1963) 31

40) Flory, P.J.; "Principles of Polymer Chemistry" 8th ed. Cornell Univ. Press., London (1971) pp. 310-313, 432-493, 595-637

41) Bevington, J.C.; "Radical Polymerization", Academic Press, London (1961) pp 58-61

42) Rouse, P.E.; J. Chem. Phys. 21 (1953) 1272

43) Ferry, J.D., et al.; J. Phys. Chem. 58 (1954) 987

44) Florea, et al.; CA 65: 10739h

45) Wagner, R.H.; J. Poly.Sci., 3 (1947) 21

46) Dixon - Lewis, G.; Proc. Roy. Soc., (London) A198 (1949) 510

47) Matsumoto, M., & Y. Ohyanagi; J. Poly. Sci., 46 (1960) 520

48) Stein, D.J.; Makromol. Chem. 76 (1964) 170

49) Jenkins, A.D.; (editor); "Polymer Science, materials Science handbook", Vol. 2, North-Holland Publ. Co., Amsterdam (1975) pp 1500-1504

50) Jenkins, A.D., (editor) Ibid, Vol.1 p. 215

51) Madorsky, S.L., J. Poly. Sci., 11 (1953) 491