

EFFECTS OF ADDITIVES ON BULK PROPERTIES OF PROCESSED PVC

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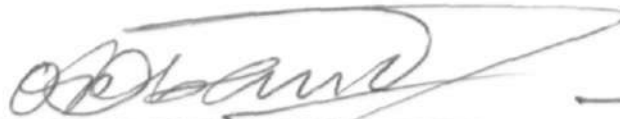
DECLARATION.

This thesis is a report of the research work carried out by me as part of the requirements for an award of a Master of Science degree in Ahmadu Bello University. The work has never been submitted elsewhere for the award of any higher degree or diploma. All the literature consulted in the course of this study have been duly acknowledged in the text by means of references.

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CERTIFICATION

This thesis entitled EFFECTS OF ADDITIVES ON BULK PROPERTIES OF PROCESSED PVC by Evelyn O. Ogode, meets the regulations governing the award of the degree of Master of Science of Ahmadu Bello University, and is approved for its contribution to knowledge and literary presentation.



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To the most high God,
Who through my sisters:
Mrs. Violet Okpaudi,
Mrs. Helen Akpokiere, and
Ms. Ethel Ogode,
made this ambition a reality.

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ABSTRACT

Flexible and rigid PVC compounds were formulated and blended with the aid of a laboratory Warring blender or a Banbury mixer. The formulations were then pressed into thin sheets using a hydraulic press.

Tensile tests were carried out on the pressed sheets to investigate both the effect of mixing shear regime and of filler type on the tensile properties of the sheets. Solvent sorption and specific gravity measurements were also carried out to correlate the trends established by the tensile properties with changes in the molecular order of the sheets as filler concentration increased.

It was observed that a high mixing shear regime enhanced the tensile properties of the sheets at the initial stages of incorporation of the fillers. The fillers namely calcium carbonate, carbon black and zinc stearate influenced the tensile properties to varying degrees. Carbon black had the most influence while calcium carbonate had the least influence. The influence of zinc stearate on the tensile properties was two-phased, with the first phase corresponding to that of carbon black and the second to that of calcium carbonate.

The effect of the fillers on the tensile properties was supported by a four-stage action on the polymer matrix. This action resulted in changes in the molecular order of the sheets with increasing filler concentration.

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ABBREVIATIONS AND SYMBOLS

PVC	-	Polyvinyl Chloride
PPVC	-	Plasticised PVC
UPVC	-	Unplasticised PVC
CC	-	Calcium carbonate
CB	-	Carbon black
ZS	-	Zinc stearate
LUC	-	Low shear CC-filled UPVC
LUB	-	Low shear CB-filled UPVC
LUZ	-	Low shear ZS-filled UPVC
LPC	-	Low shear CC-filled PPVC
LPB	-	Low shear CB-filled PPVC
HUC	-	High shear CC-filled UPVC
HUB	-	High shear CB-filled UPVC
HPB	-	High shear CB-filled PPVC
PE	-	Polyethylene
DINP	-	Disononyl phthalate
DBLS	-	Dibasic lead stearate
Ba/Cd/Zn	-	Barium/Cadmium/Zinc
K-value	-	Molecular Weight Parameter
T _g	-	Glass transition temperature
T _m	-	Crystalline melting temperature
Phr	-	Parts per hundred parts of resin
rpm	-	Revolutions per minute
%	-	Percent
°C	-	Degree celcius
mm	-	Millimetre
nm	-	Nanometre
micron	-	Micrometre
g	-	Gramme
cm ³	-	Centimetre cubed
g/ml	-	Gramme per millitre
mm/min	-	Millimetre per minute
mPa	-	Mega Pascals
N/m ²	-	Newton per metre squared
YS	-	Yield stress
FS	-	Fracture stress
SG	-	Specific gavity
ES	-	Equilibrium sorption
EB	-	Elongation at break
ASTM	-	American Society for Testing of Materials.

CHAPTER ONE

INTRODUCTION

Polyvinyl chloride (PVC) is a widely used plastic material with diverse applications. The resin is commercially available as a free-flowing white odourless powder. When processed without stabilisers, the resin degrades readily, turning from yellow through brown and finally to black when fully carbonized. In its pure state, the processed material is hard and brittle but when plasticized, the product becomes soft and flexible.

Unplasticized PVC (UPVC) is impervious to most dilute and concentrated acids, alkalis, oils and alcohols. However, it is attacked by some organic solvents which swell or dissolve it. Plasticized PVC (PPVC) also resists chemical attacks but to a lesser extent than UPVC, Swanson (1965).

When heated, PVC begins to soften at about 80°C and at above 140°C, it loses all its mechanical strength. If heated to between 170°C and 180°C, PVC decomposes and evolves gaseous hydrochloric acid. For this reason, the resin is formulated with heat stabilisers to facilitate processing, Todd (1972).

According to Swanson (1965), the most important methods of processing UPVC are injection moulding and extrusion while compression moulding and calendering are widely used for

processing the plasticized resin.

1.1 History of PVC

The first definite report of the production of PVC was around 1860 according to Kaufman (1969). However, between that time and just before the world wars, much progress was not made because of the instability and rigidity of the pure resin. Tester (1973) reports that attempts were made in the 1920s to produce copolymers of PVC with other available plastics but it was not until around 1930 that the first significant breakthrough was achieved.

PVC was first produced in commercial quantities in Germany, in 1937. According to Tester (1973), during the First World War, due to shortages of metal and wood, especially in Germany, much attention was focused on PVC and this led to a tremendous rise in the production of the resin. In the United Kingdom, PVC was first produced commercially at the outbreak of the Second World War.

1.2 Production of PVC

The monomer of PVC, that is, vinyl chloride, is a gas which boils at -140°C . It is produced in a two-stage process in which ethylene is first reacted catalytically with hydrochloric acid and oxygen to yield 1,2-dichloroethane which is then pyrolysed to give vinyl chloride and hydrochloric acid, the latter is

recycled, Billmeyer (1971).

The vinyl chloride is polymerised to give PVC and this can be done using any of the traditional polymerisation techniques. The techniques include, suspension, emulsion, bulk and solution polymerisations. Suspension polymerisation is the most common and it accounts for most of the PVC materials used for moulding, extrusion and calendaring processes. Emulsion polymerisation is next in importance and is widely used to produce the PVC used in plastisols and organosols. Bulk and solution polymerisation have little commercial significance, Billmeyer (1971).

1.3 Pattern of PVC usage

PVC is perhaps the most widely used of all plastics in the world today, Tester (1973). It is a versatile plastic primarily because it can be modified to produce compounds having an almost infinite number of diverse properties, Lutz (1974). PVC may be varied from fully rigid to highly flexible forms and these encompass a wide range of applications such as cables, flooring, leather clothings, flexible and rigid films and sheets, bottles and phonograph records.

It is also used in the production of footwears, rigid and flexible pipes and in fabric and paper coatings. It is used in slush moulding, plastisol rotational castings, calendaring, injection moulding and extrusion. This is the reason why PVC has

developed so rapidly and why it is such a good outlet for additives, King (1972).

PVC films and sheets are seen in end products like rainwears, shower curtains, toilet bags, shower caps and food covers. A large amount of PVC-coated fabric is used for upholsteries, Billmeyer (1971).

1.4 Aim of this present Research Work

The properties of PVC products are controlled by a variety of structural factors which in turn are influenced by formulation and processing conditions, Gilbert and Ansari (1982). It is also known that the morphological changes which PVC undergoes during processing are dependent on both temperature and level of shear, Obande and Gilbert (1989). Mckinney (1965) adds that PVC processing is affected by additives which are incorporated into its formulations.

The present work forms part of a project aimed at investigating the structure - property relationships of processed PVC. In this work, PVC will be processed with three different fillers, namely calcium carbonate, carbon black and zinc stearate. The effect of these fillers on some physical properties of the polymer will then be investigated using a number of techniques. The effect of shear will also be investigated by using low and high shear mixing equipment.

CHAPTER 2

LITERATURE SURVEY

In examining the structure-property relationship of PVC, it is necessary to understand its structural make-up and the effect of processing on the structure.

This survey will therefore highlight the literature account of the structure of PVC and the effect of processing on the PVC structure. Since PVC is always invariably processed with additives, the survey will also extend to the effects of additives on the processing of PVC. Finally, some methods of examining structure-property relationships will be reviewed.

2.1 Structure of PVC

PVC is a vinyl polymer, made up of $[\text{CH}_2\text{-CHCl}]$ repeat units. It is a partially syndiotactic and slightly crystalline polymer. It is believed that the crystallinity is related to the presence of short syndiotactic sequences which give rise to small regions within the polymer, Mammi and Nardi (1963), Neilson and Jabarin (1975).

Like other polymers, the structure of PVC consists of both the internal arrangement of the chains and the way they are packed together. And the macrostructure or supermolecular structure is the three-dimensional arrangement of the polymer

chains.

2.1.1 Microstructure of PVC

In terms of microstructure, PVC is referred to as a semicrystalline polymer, that is, it has both a crystalline phase and an amorphous phase. Hence, PVC has a glass transition temperature (T_g) which is associated with the amorphous phase and also a melting temperature (T_m) associated with the crystalline phase. The T_g of PVC is 80°C while the T_m is 220°C as noted by Mills (1988).

The first indication of crystallinity in PVC was reported by Natta and Corradini (1956), several workers, after them, have confirmed this claim. Pezzin (1971) determined the level of crystallites to be between 5-10% Illers (1977) has shown that the crystals in PVC do not all have the same size, instead they show a size distribution, this is why PVC melts over an unusually wide temperature range. Mills (1988) explained further that the crystals bind the PVC particles together so that crystalline fusion does not result in a homogeneous melt at the normal processing temperatures.

2.1.2 Supermolecular structure of PVC

The supermolecular structure of PVC can be said to be a three-dimensional network where the microcrystallites are believed to act as cross linkages between the polymer chains, Jackson et al. (1963), Shen and Tobolsky (1965), Gilbert and Ansari (1982). This structure is however complicated by the possibilities of chain branching and the tendency of the polymer to associate in solution, Billmeyer (1971).

The knowledge of the structure of PVC gives an insight into the melt flow behaviour of the polymer rheological pattern of flow to expect during PVC processing at different temperatures.

2.2 Processing of Plastics

Well-designed plastic articles are not made by simply cutting and fastening plastic materials as is done with wood and metal, instead the plastic is heated until it softens, after which it is forced into any desired shape, Swanson (1965).

Heat transfer is a major aspect of plastic processing. The main heat transfer processes encountered in the processing of plastics are conduction, convection and viscous heating and to a lesser extent, radiation, Mills (1988). Shear stress and

shear strain rate influence the heat transfer quantitatively.

The melt characteristics of plastics are quite different from those of other materials, due to the differences in their structures. In the melt, molecules of the plastic are packed closely together with Van der Waal forces between the polar or non-polar groups in neighbouring molecules. These molecules are knotted around each other to give entanglements. Crystals are also present within the matrix of the plastic, these crystals bind the molecules together. Mills (1988) explains that the application of heat to PVC does not result in a homogeneous melt because of the presence of crystals in the matrix of the plastic.

During processing, several types of melt flows occur, these are shear flows, extensional flows or a combination of both. These flows result in the deformation of the particles of the plastic and hence the structure of the plastic being processed.

2.2.1 Processing of PVC

Most of the PVC resin used for melt processing is made by suspension polymerisation according to Mills (1988). Suspension polymerisation gives rise to PVC with grains that are roughly spherical with an internal porosity. However, during processing, there is a breakdown of the grain structure of PVC

and an elimination of the porosity of the grains.

The initial stage of processing occurs once the PVC is heated above its T_g of 80°C , the grains are compacted together and this increases bulk density. At this stage, the various solid additives are at the grain boundaries. As the density increases, the porosity of the grains reduces, the grains then become deformable and elongate in the direction of melt flow. In the final stage, the grain boundaries fuse and a melt containing only the primary particles is left, Mills (1988).

The breakdown is not the same if the PVC powder was compounded in an internal mixer, in which case, the grains will have been broken into fragments by reason of a higher level of shear at an early stage in the process. In the final stage, a continuous entanglement network is formed, this entanglement network is made more effective as the crystallites bind neighbouring molecules together, Portingell (1982).

The processing of PVC should give rise to articles with high fusion and gelation levels. If the processed articles have weak grain boundaries, these will constitute themselves into sites where cracks will be easily formed if stresses are applied. Continuous application of such stresses would lead to catastrophic crack growth and eventual failure.

An understanding of the effect of processing on the particulate nature of plastics, an example of which is PVC, is invaluable in the determination of structure-property relationships of processed plastic articles, since any alteration in the structure will affect the properties of the plastic.

The properties of plastic articles are also affected by the type of additives that are added to the plastic resins. Hence there is a need to exercise care in the choice of additives and of processing conditions in order to reduce the risk of producing poor quality articles.

2.3 Additives for PVC

The term additive is used to describe any material which can be physically dispersed in a polymer matrix without significantly affecting the molecular weight of the polymer, Mascia (1974). The most important requirement of an additive is that it should be effective at an economic level, for the purpose for which it was incorporated into the polymer.

PVC in its pure state is almost of no consequence. It is hard and brittle and is also extremely susceptible to rapid degradation. It is relatively unstable to heat and light, which readily initiate degradative reactions in the polymer. These reactions result in the loss of hydrochloric acid and in the

formation of polyene structures within the polymer. In the presence of oxygen, the degradative reactions are accelerated and ketonic structures are formed in the polymer, Billmeyer (1971).

Additives are always invariably added to PVC, to improve its stability and resistance to degradation. Additives are also incorporated into PVC to confer some desirable qualities. These qualities will differ according to the type of additive but generally, the addition of an additive to PVC will enhance its physical properties.

A wide range of materials are available as additives. When classified according to their specific function, two main groups arise. The first group comprises those that achieve their effect by modifying the physical properties of the polymer, among which are plasticisers, lubricants and fillers. The other group consists of those that achieve their effect by chemical reactions, among which are stabilisers and flame retardants, Mascia (1974).

2.3.1 Stabilisers

Stabilisers are substances added to polymer to stop or reduce the rate of degradation induced by heat, light, oxygen, ozone, high energy radiation or other environmental factors, Todd (1972) and Mascia (1974). Stabilisers achieve their effect

either by intervening in the degradative reactions of the reactive species to give inactive species, or by removing or deactivating or promoting competition for sources that have catalytic action on the degradative process, Nass (1976).

There are different types of stabilisers. The first group are the heat stabilisers which are commonly used in PVC and related copolymers. They accept any hydrochloric acid evolved from the polymer and also react with the double bonds formed during breakdown, to prevent the formation of conjugated polyenes. Antioxidants are another group of stabilisers, they suppress oxidative degradation reactions by acting as radical acceptors and peroxide decomposers. Antiozonants react with ozone or ozonides and thus prevent the degradation that their reaction with the polymer will have caused. Similarly, ultra violet absorbers absorb ultra-violet radiation and hence prevent the degradation that its reaction with the polymer will have caused, Todd (1972).

2.3.2 Lubricants

Lubricants are substances which are added to polymeric materials in order to assist their processing. The most obvious role of lubricants in PVC processing is to improve slip between molten PVC and die surfaces. But the most critical function is the control of PVC melting rate, this, the lubricant achieves by influencing the rate at which PVC powder melts and the

mechanical heat or shear developed in the processing equipment, Gale (1973).

The exact amount and type of lubricant to be used in a given polymeric system can be determined only by trial and error since these factors are determined by the type of processing, the equipment, the operating conditions and the surface to volume ratio of the product, as noted by Todd (1972).

However, it is necessary to achieve a balance between the amount of lubricant needed to facilitate processing and the amount that will constitute over or under lubrication. Overlubrication can cause haze in clear products, embrittlement of rigid products and delamination of moulded products, while underlubrication results in poor surface finish of the product.

2.3.3 Plasticisers

A plasticiser is a substance which, when incorporated into a polymeric material, will increase its flexibility, workability and distensibility and will also alter its temperature dependent properties such as T_m and T_g , Coulson (1972). Plasticisers achieve their effect by neutralizing the Van der Waal forces between the polymer chains, thereby increasing the mobility of the chains, Gould (1965).

Plasticisers are generally grouped into phthalates, phosphates, low temperature diesters, polymeric plasticisers, epoxides and others, Foakes (1973). The phthalates are the most widely used because they confer a reasonable proportion of the qualities required in a majority of industries but they are rather volatile. The phosphates are less volatile and are also more resistant to extraction than the phthalates, both groups are highly compatible with polymers. Others are the adipates and sebacates which do not possess high compatibility but are good for low temperature applications. Polymeric plasticisers are not as efficient as the other examples but they have a high degree of permanence.

2.3.4 Fillers

Fillers are substances which are incorporated in polymers to improve their general properties, introduce some particular characteristics or simply reduce cost, King (1972). For instance, the prime reason for the use of fillers in PVC is to reduce cost. Fillers have also been defined by ASTM D-20, as relatively inert materials which are added to plastics to modify physical properties, Binji (1990).

Most fillers are classified on the bases of the size and shape of the filler particle and its surface area. The choice of a filler is therefore determined by its particle size and

shape as well as the manner in which the particles pack themselves together. The choice can also depend on the end use of the article to be processed, Mailabari (1988).

In addition to reducing cost, fillers are required in PVC to confer surface finish properties, improve resistance to scratching and reduce tack. One of the most widely used fillers in PVC is calcium carbonate, it is used in the form of natural whittings, precipitated or fatty acid coated forms, King (1972).

2.4 Properties of PVC

The ultimate properties of PVC, like other plastic materials, are determined not only by the structure of the pure unprocessed resin, but also by the resultant effect of additives and of mode of processing on the structure, as stated earlier on. Thus the properties of processed PVC articles will vary with type of additives and mode of processing.

In its pure state, PVC has flame resistance properties due to the presence of the chlorine atom in its repeat unit. PVC also has a high volume resistivity in the region of over 10^{16} Ohm as noted by Deanin *et al.* (1965). However, the addition of plasticisers and other additives reduce its flame resistance and volume resistivity.

The molecular and supermolecular structure of PVC make it

excellent in chemical resistance. It is also excellent for electrical insulating applications at low frequencies. However, at high frequencies, PVC will conduct electricity due to its polar nature.

Like other semicrystalline polymers, PVC possesses both a T_g and a T_m . Below and around the T_g , PVC has the characteristics of glass. Above T_g but below T_m , PVC exhibits properties of rubbery materials, and above T_m , PVC is molten and behaves like a high viscosity fluid, Shen and Tobolsky (1965).

At ambient temperatures, that is below T_g , UPVC is a tough thermoplastic with low tensile strength. It is relatively unstable to heat and light and will undergo decomposition with the evolution of hydrochloric acid if it is heated to about 170°C or if exposed to ultraviolet light.

A knowledge of the properties of polymers is important in their characterization. Since characterization is based on the properties of a substance, among other criteria. Hence for complete characterization, the properties of a polymer should be known.

2.5 Characterization of PVC Bulk

Phase Structure

Polymer characterization is of very great importance, its scope can be relatively narrow or extremely broad depending on the degree of scientific and commercial interest that the polymer, under examination, generates. Initial characterization can be considered in two wide categories, these are molecular structure and physical properties.

An indepth molecular structure of polymers can be obtained by both chemical and physical methods. Methods of characterizing physical properties are in two categories, the first is elementary and it defines the properties of a given polymer. The second defines the uses of a polymer, Sorenson (1965). The chaacterization of physical properties, in both cases may provide information on some fundamental properties of the polymer or may be entirely empirical.

There are several types of characterization methods, among these are hardness tests, comprssion tests, flexural and tensile tests. Others are solvent sorption, density measurements, flame, oxygen and ozone resistance tests. The methods applicable to the present study are reviewed below.

2.5.1 Solvent Sorption

This is one of the characterization methods that aims at assessing the molecular structure of polymers. The objective here is to determine the effect of a solvent on a polymer under investigation, Billmeyer (1971). A solvent which can swell the amorphous regions of a polymer but will not dissolve the crystallites, is used to detect differences between polymers and to establish their molecular structure, Gilbert and Mulla (1983).

The transport of solvents through polymers involve a diffusion process which is controlled by both a concentration gradient and a relaxation process. The relaxation process of diffusion is due to the time dependent response of the polymer chains to the swelling stress, Berens (1977). As the relative contributions of these two processes change and interact, a wide range of behaviour can be encountered.

Several workers have used solvent sorption to characterize polymers. Gray and Gilbert (1976) used it to differentiate between three types of PVC compounds, they also used it to investigate the relationship between thermal history, crystallinity and physical properties of PVC compounds containing different types and levels of additives. Gilbert and Mulla (1983) used solvent sorption to detect structural

changes in rigid PVC compounds, they suggested that sorption is controlled by the amount of crystallinity present in a sample.

Obande and Gilbert (1989) used solvent sorption, among other techniques to investigate crystallinity changes that occur in PVC compounds during processing, they concluded that equilibrium sorption is dependent on amount of crystallinity and that sorption will only occur in the amorphous regions of polymers. Sorption has also been reported to depend on the gelation level of samples, Obande et al. (1993).

2.5.2 Density Measurement

This is a characterization method that assesses the physical properties of polymers. Physical properties are arbitrarily divided into two, those that categorize a material broadly and those that define it specifically. Density belongs to the first category.

The density of a polymer may in some cases be critical to the ultimate end-use potential since a low density polymer will obviously occupy more volume. In any event, density can add to the basic understanding of a material in every instance, Sorenson (1965).

Sheldon (1963), Gray and Gilbert (1976) and, Obande and Gilbert (1989), have used density to estimate crystallinity changes in polymers. They explained that a density increase can

generally be construed to mean a definite increase in crystalline content.

Much earlier Sperati et al. (1953) had measured the crystallinity of polyethylene (PE) samples using density. They suggested that density could be related to stiffness, yield point and sorption of reagents. They suggested further that density directly controls ultimate elongation and hardness.

However, for PVC density has been observed to be also dependent on both time and processing temperature, Gray and Gilbert (1976) and Obande and Gilbert (1989). They observed that density increases with a corresponding increase in processing temperature.

2.5.3 Tensile Tests

This characterization method also assesses the physical properties of polymers. The physical properties considered here are those that categorize a polymer specifically. Tensile tests are based on the tensile properties of a polymer, these properties, with other mechanical properties determine the end uses and the limitations of such a polymer, Sorenson (1965).

Normally, tensile tests are performed by assessment of the stress-strain behaviour. Here a specimen of some standard shape and dimensions is subjected to a stress applied at some

determined rate, a recorder, attached to the testing instrument gives a plot of the force required to produce a given elongation.

The stress-strain plot shows at once, the absence of a yield point, the slope of the initial portion of the curve can be used to calculate an elastic modulus in tension. The modulus is related to the stiffness and resistance to deformation of the polymer. The overall shape of the curve reveals whether the material is basically brittle or ductile. A brittle material shows a relatively low elongation at break and a steep initial portion in the stress-strain curve. Also, a brittle material does not yield. A ductile material, on the other hand, exhibits a yield point and a relatively high elongation at break. A typical stress-strain plot is shown in Figure 2.1.

According to Harris (1969), the tensile properties of polymers, not only define the quality of production lots of polymeric materials as well as their design and engineering behaviour, they also indirectly measure other properties of the material for which a correlation exists. For example, a plastic film having high tensile strength and elongation in all directions will probably also have high impact strength. Tensile properties may also be used to monitor chemical or physical changes taking place in a polymer.

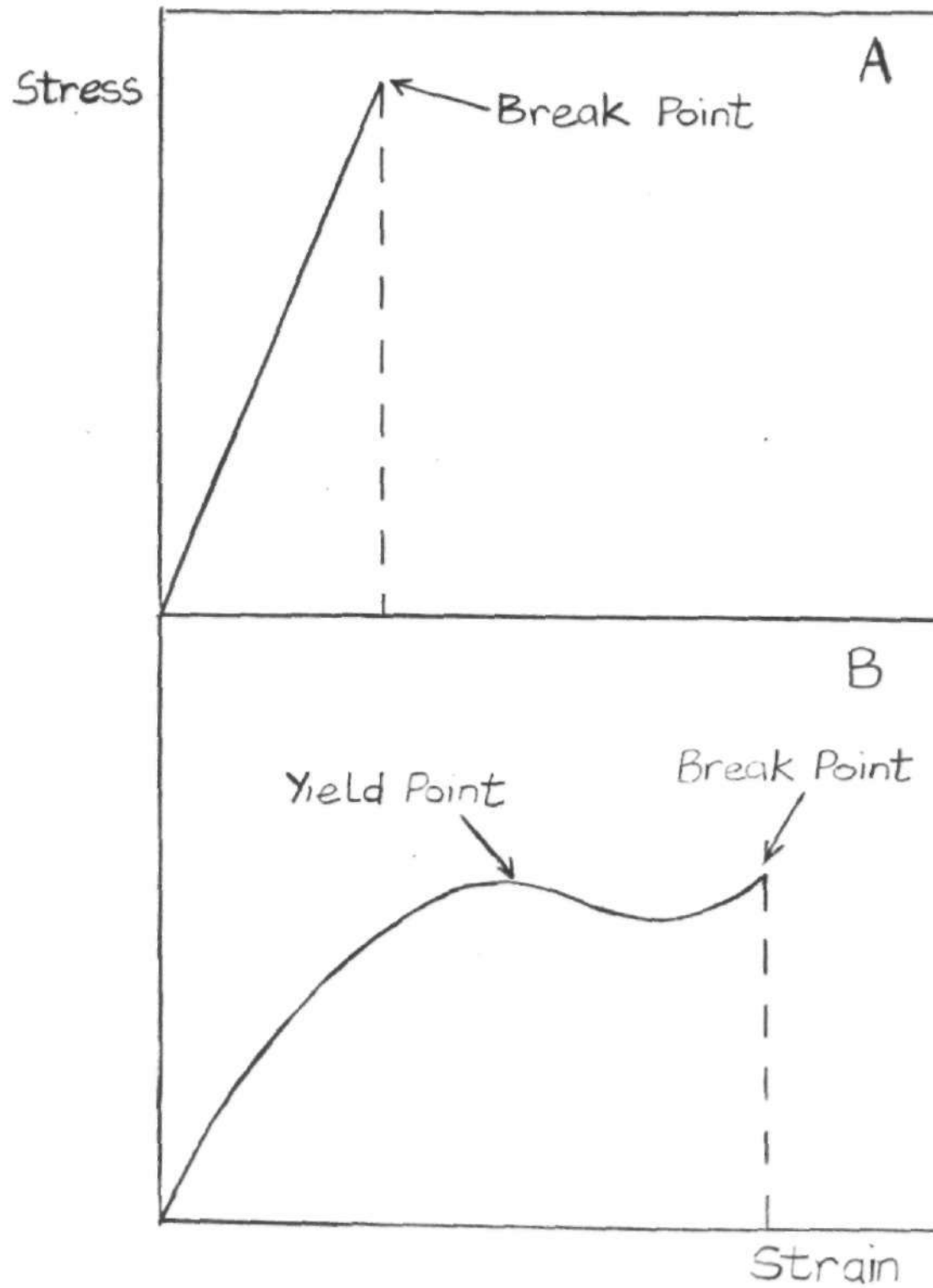


FIGURE 2.1
A typical stress-strain plot showing a variation of stress with strain.
A=Brittle Material; B=Ductile Material

Pezzin et al (1972), from their determination of stress-strain relationships in PVC using uniaxial tensile tests have suggested that pre-yield deformation is not significantly affected by processing temperature but that stress and strain at break are greatly affected by processing temperature. The extent of this influence on the post yield deformational behaviour of PVC is determined by the ability of the material to cold draw.

Before PVC samples undergo yielding, the material becomes locally unstable at regions of high stress concentration and at a critical strain level, local dilatational yielding occurs and crazes are formed. According to Bucknall (1977), the propagation of such crazes continue until the formation of band of shear yielded material which terminate the growth of the craze. Newman and Stella (1965) explain further that crazing increases the total free-volume of the polymer and also lowers its T_g so that necking or cold drawing occurs, this continues until the material eventually fractures.

Yield stress varies significantly with both temperature and strain rates. This is in agreement with experimental observation made by Andrews (1968), he supported the concept of yielding as a basically viscoelastic phenomenon. Kausch (1978) showed that shear yielding is dependent on temperature. This temperature dependence accounts for the sensitivity of the post

yield stress and strain to processing temperature as noted by
Pezzin et al. (1972)

CHAPTER 3

EXPERIMENTAL PROCEDURES

The experimental procedures involved in this project work can be divided into two major parts. These are sample preparation and the analysis of the samples. The samples were prepared by first compounding the PVC-additives formulations to give homogeneous blends. These blends were then compression moulded into sheets.

The analysis of the PVC sample sheets carried out by cutting them into required sizes and shapes and then carrying out the tests on the cut specimens.

3.1 Equipment

The major equipment used during this research work are listed in table 3.1.

3.2 Materials

All the materials used for this work, their description and their sources are listed in Table 3.2.

Table 3.1. Equipment used and their sources.

S/No	Equipment	Manufacturer
1.	Mettler H31 Analytical Balance	Gallenkamp, England
2.	Laboratory Warring Blender	Moulinex, France
3.	Banbury Mixer	Farrel Bridge Limited Lancashire, England
4.	Hydraulic Press	George E. Moore & Sons Limited, Birmingham, England
5.	Instron Tester	Instron Limited, England
6.	Micrometre Screw Gauge	GKN Shardow Metrology Limited, Sheffield, England
7.	Specific Gravity Bottles	Quickfit, England.

3.3 Sample Preparation

The preparation of the samples involved two stages. The first stage was the mixing of the PVC resin with the additives to give dry blends. The second stage was the moulding of the PVC-additives blends into thin sheets. However, before the mixing was carried out, the different formulations were first prepared.

Table 3.2: Description and sources of materials used.

S/No.	Material	Description	Source
1.	PVC resin	White particulate solid K-value = 68 Particle size < 315 nm Density = 0.56g/cm	Manufactured by Shintech, Houston, Texas.
2.	Plasticiser- Disononyl Phthalate(DINP)	Clear liquid Density = 0.97g/cm ³ Viscosity at 20°C = 105mPa Refractive Index = 1.487	Supplied by PVC Compounders Kaduna
3.	Fillers		
a.	Calcium carbonate	White particulate, solid Density = 2.7g/cm ³ Particle size = 1-2 micron Percentage purity = 99.85	Supplied by PVC Compounders Kaduna
b.	Carbon Black	Black Particulate Solid Particle size = 350-700nm Specific Gravity = 1.8 - 2.1	Manufactured by Sico-Echswartz West Germany
c.	Zinc Stearate	Fluffy White Powder Melting point = 120°C Specific Gravity = 1.09 Free Fatty Acids = 0.5%	Manufactured by Ventron GMBH Germany
4.	Stabilisers		
a.	Barium/Cadmium/ Zinc salt (Ba/Cd/Zn)	Clear Liquid Density = 1.15g/cm ³ Flash Point = 93°C Viscosity at 23°C = 190mPa	Supplied by PVC Compounders Kaduna
b.	Dibasic Lead Stearate (DBLS I)	White Powdery Solid Specific Gravity = 0.7 Metal content = 50-52% Free Fatty Acids = 1%	Supplied by PVC Compounders Kaduna
c.	Dibasic Lead Stearate (DBLS II)	White rod-like pellets Metal content = 50-52% Free Fatty Acids = 1%	Supplied by Mutunci Company Kaduna

Table 3.2: Description and sources of materials used (cont'd.)

S/No.	Material	Description	Source
5.	Lubricant-Stearic Acid	White crystalline solid Molecular weight = 284.49g Melting point = 70°C Percentage Purity = 99%	Supplied by PVC Compounders Kaduna
6.	Solvent-Acetone	Clear Liquid Molecular weight = 58.08g Percentage Purity = 99%	Manufactured by BDH Chemicals Ltd, Poole, England

3.3.1. Formulations

Eight sets of formulations were used during this research work, each set consisted of ten different formulations. Five of these sets were low shear mixed and out of these, two sets were plasticised. The remaining three sets were high shear mixed and one of these sets was plasticised. Tables 3.3 and 3.4 give the details of the low shear formulations, while Tables 3.5 and 3.6 give those of the high shear formulations. Table 3.7 gives the variation of filler concentration within each set of formulations.

Table 3.3: Low shear unplasticised formulations.

Material	Concentration (g)
PVC resin	100
Filler*	0 - 10
Ba/Cd/Zn	2.0
Stearic Acid	0.5

* Fillers used were calcium carbonate, Zinc stearate and carbon black respectively.

Table 3.4: Low shear plasticised formulations.

Material	Concentration (g)
PVC resin	100
Filler*	0 - 10
Ba/Cd/Zn	2.0
Stearic Acid	0.5
DINP	50

* Fillers used were calcium carbonate and carbon black respectively.

Table 3.5: High shear unplasticised formulations.

Material	Concentration (g)
PVC resin	1000
Filler*	0 - 100
DBLS I	10
DBLS II	15
Stearic Acid	5

* Fillers used were calcium carbonate and carbon black respectively.

Table 3.6: High shear plasticised formulations.

Material	Concentration (g)
PVC resin	700
Filler*	0 - 70
DBLS I	7.0
DBLS II	10.5
Stearic Acid	3.5
DINP	350

* Carbon black was the only filler used in these formulations.

Table 3.7: Variation of fillers concentration.

Formulation Variation	Filler Concentration (phr)
1	0
2	0.05
3	0.10
4	0.30
5	0.50
6	1.00
7	1.50
8	3.00
9	5.00
10	10.00

3.3.2 Mixing

Two types of mixers were used. The first was a laboratory Warring blender used for the low shear mixing while the other was a Banbury mixer which was used for the high shear mixing.

In the mixing of the low shear formulations, the PVC and additives were charged into the mixing chamber of the blender, and the impeller set into motion. Mixing was done intermittently for 15 minutes, the final temperature of the polyblend was $55 \pm 2^\circ\text{C}$. For the plasticised formulations, the plasticiser was added after 5 minutes of mixing and the total mixing time was 20 minutes.

In the mixing of the high shear formulations, the PVC resin and additives, including the plasticiser for the plasticised formulations, were charged into the mixing chamber of the Banbury mixer and the rotors set into motion at a speed of 80 rpm. The duration of mixing was 10 minutes. The final temperature of the unplasticised polyblend was between $30 - 40^\circ\text{C}$ and that of the plasticised variation was between $50 - 60^\circ\text{C}$.

3.3.3 Compression Moulding

The compounded PVC blends were compression moulded into

thin sheets using a 20 ton more Hydraulic press.

For the unplasticised polyblend, about 5g of the mixture was weighed and transferred to a preheated mould which was covered with aluminum foil. The mould was then inserted into the press. the operating temperature was between 150- 160°C while the pressure was between $3.5 - 4.8 \times 10^7$ N/M². The duration of the compression moulding was 2 minutes. At the end of the moulding, the mould was removed from the press and allowed to cool in air. The solidified PVC sheet was removed from the mould after cooling.

For the plasticised blends, about 4g of the mixture was used for each compression moulding. The operating temperature was between 120-130°C while the pressure was between $5.5 - 6.2 \times 10^7$ N/M². The duration of the compression moulding was 3 minutes.

3.4 Analysis of Moulding sheets

Three methods of analysis were used to examine the compression moulded PVC sample sheets. These were solvent sorption, specific gravity determinations and tensile testing.

3.4.1 Solvent Sorption Measurement

The procedure from an earlier work by Obande and Gilbert (1989) was adopted. Specimens measuring 20 x 10 x 0.35mm were

prepared and weighed. They were then immersed in excess analytical grade acetone contained in 20cm³ stoppered glass bottles. the set up was left for 24 hours, after which, the specimens were retrieved and weighed. An average of three measurement was made for each sample.

3.4.2 Specific Gravity Determination

Specific gravity bottles were used and the determination was carried out at room temperature, between 24-26^oc. The solvent used was water. Thin strips weighing between 0.06 - 0.10g were cut from the PVC sheets. The specific gravity bottle filled with water was weighed. Next the strips of PVC were immersed in the bottle displacing some water in the process. The bottle containing both water and PVC was weighed. The weight of the displaced water was found by difference. An average of three measurements was made for each sample.

The formula used to calculate the specific gravity of the PVC sheets was adopted from discussions with Olayemi (1994).

3.4.3 Tensile Testing

The tensile testing was carried out using an Instron Model 1026 machine. The test pieces were cut with the aid of a template. The shape of the specimens was dumb bell and the

length 75mm. The sample thickness was measured with a micrometre screw guage.

The test was carried out according to ASTM D-638. The guage length was 30mm. For the unplasticised samples, the crosshead speed was 500mm /min while the chart to crosshead ratio was 4:1. For the plasticised samples, the crosshead speed was 100mm/min while the chart to crosshead ratio was 1:2. The same load cell was used for both the unplasticised and the plasticised samples.

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 Sample Coding

Altogether, eight different sets of samples were used in the course of this research work. Each set of samples consisted of ten different formulations.

The sets of samples were coded for easy identification. The two unplasticised sets of samples that were filled with calcium carbonate were coded LUC and HUC respectively. The LUC set of samples were blended using a laboratory Warring blender in order to investigate the effect of blending at low shear regime while the HUC set of samples were blended using a Banbury mixer, to investigate the effect of blending at high shear regime.

The two unplasticised sets of samples that were filled with carbon black were coded LUB for those mixed with the Warring blender and HUB for the those mixed with the Banbury mixer. Another unplasticised set of samples was filled with Zinc stearate, mixed with the warring blender and coded LUZ. The plasticised version of LUC was coded LPC, that of LUB was coded LPB and that of HUB was coded HPB. The HUC and LUZ sets of samples had no plasticised versions.

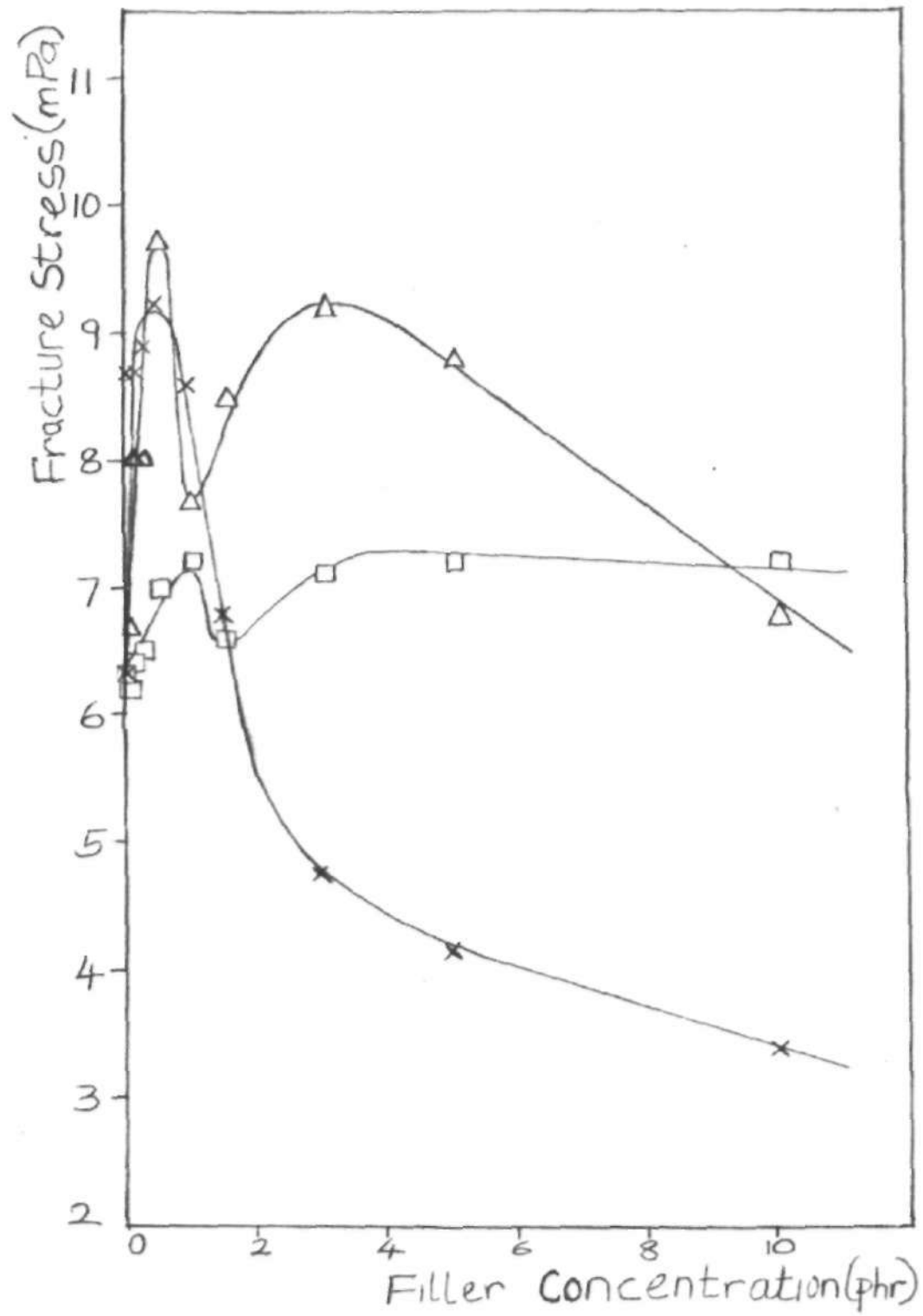


FIGURE 4.1

Variation of fracture stress
with filler concentration

□ = LUC; △ = LUB; × = LUZ

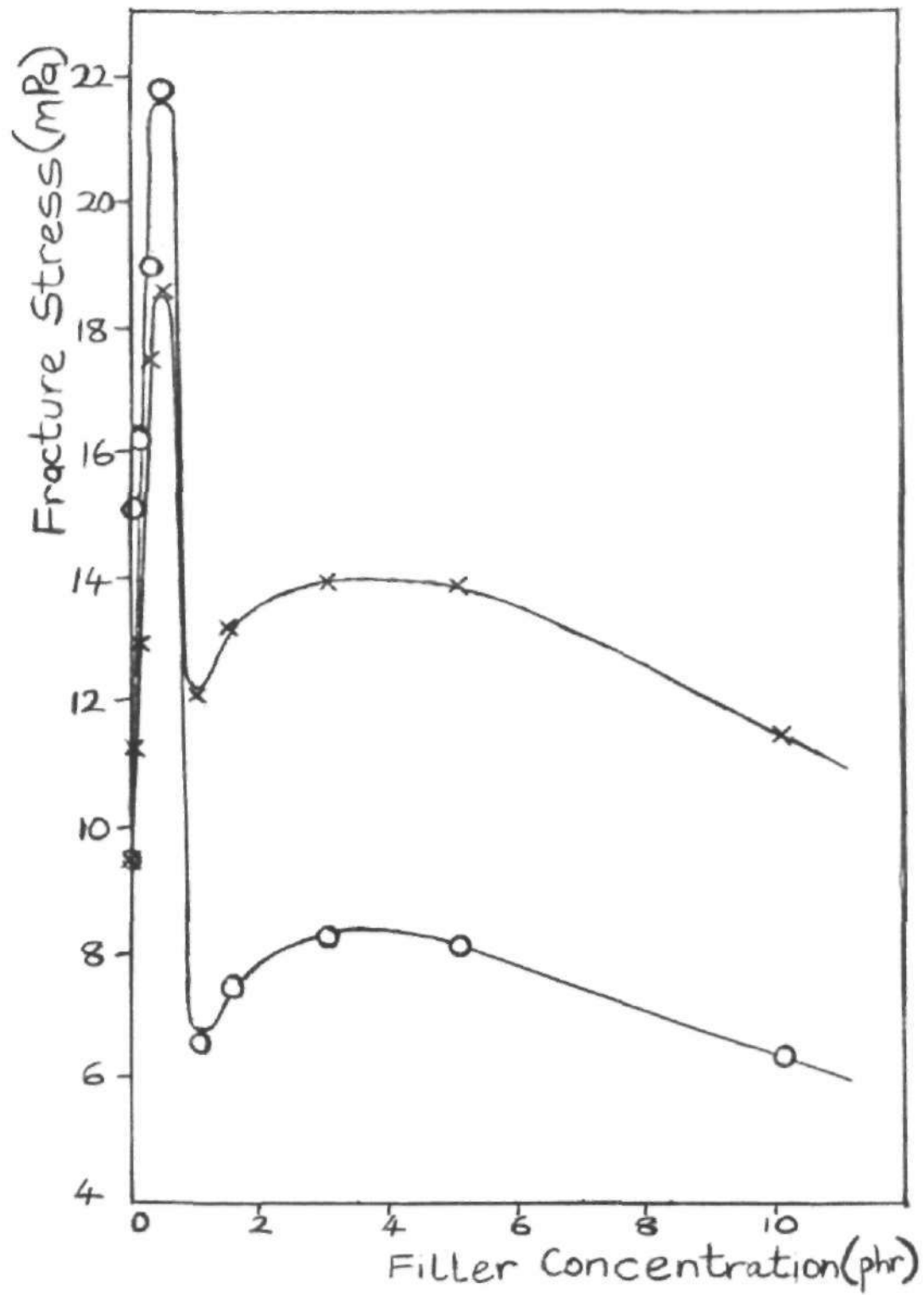


FIGURE 4.2

Variation of fracture stress
with filler concentration
x = HUC; o = HUB

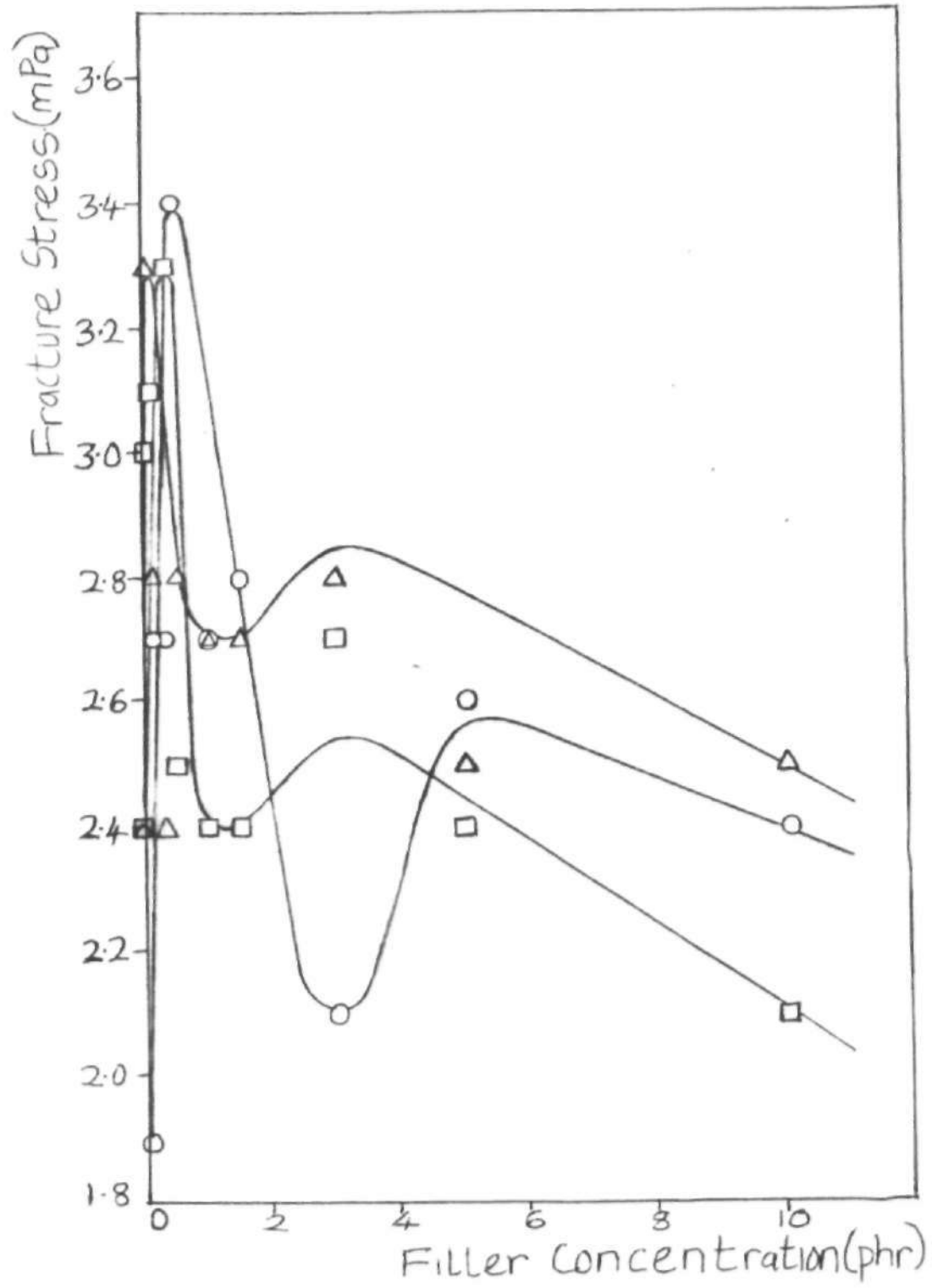


FIGURE 4.3

Variation of fracture stress
with filler concentration
□ = LPC; Δ = LPB; ○ = HPB

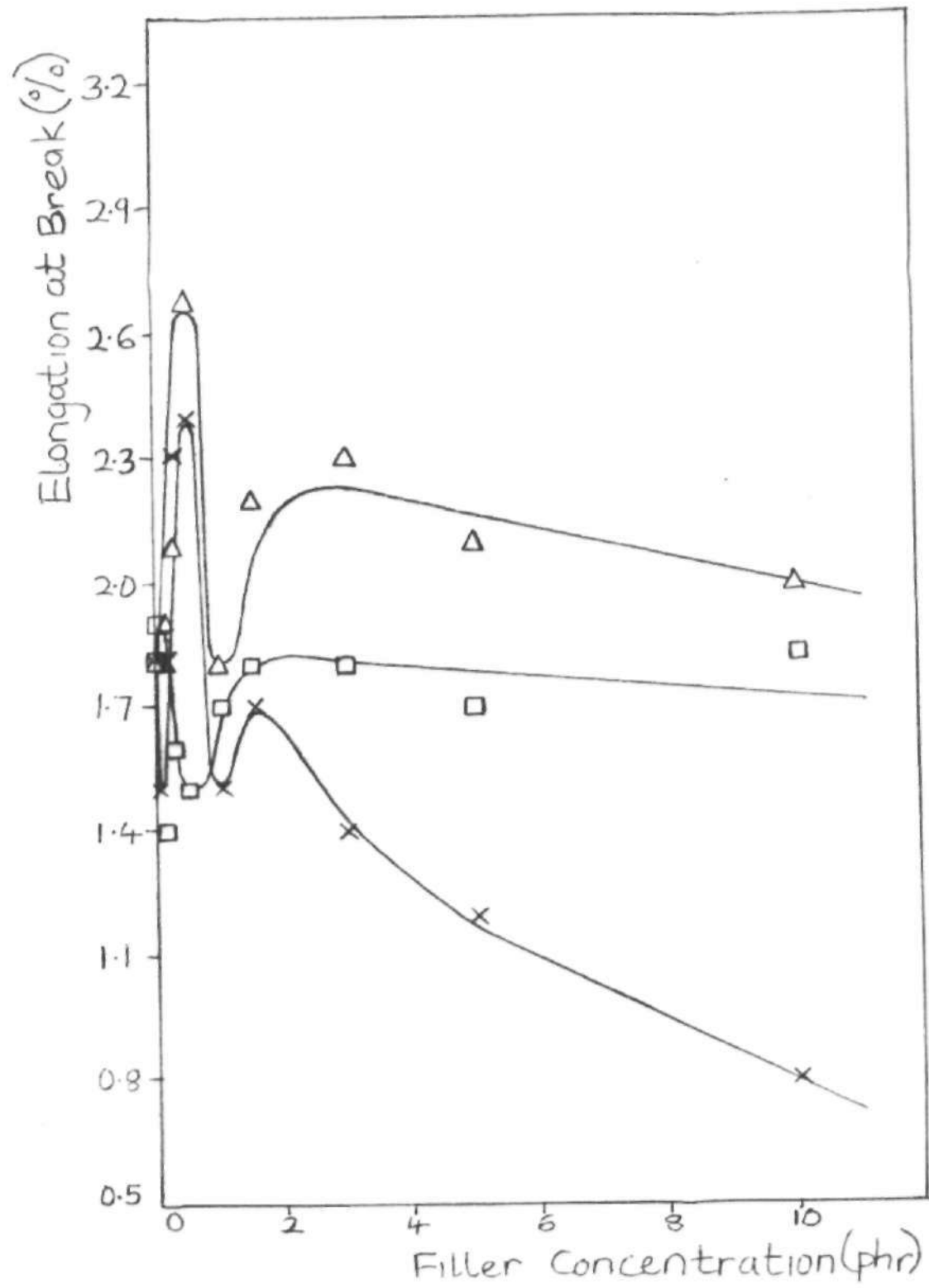


FIGURE 4.4

Variation of elongation at break
with filler concentration
□ = LUC; Δ = LUB; × = LUZ

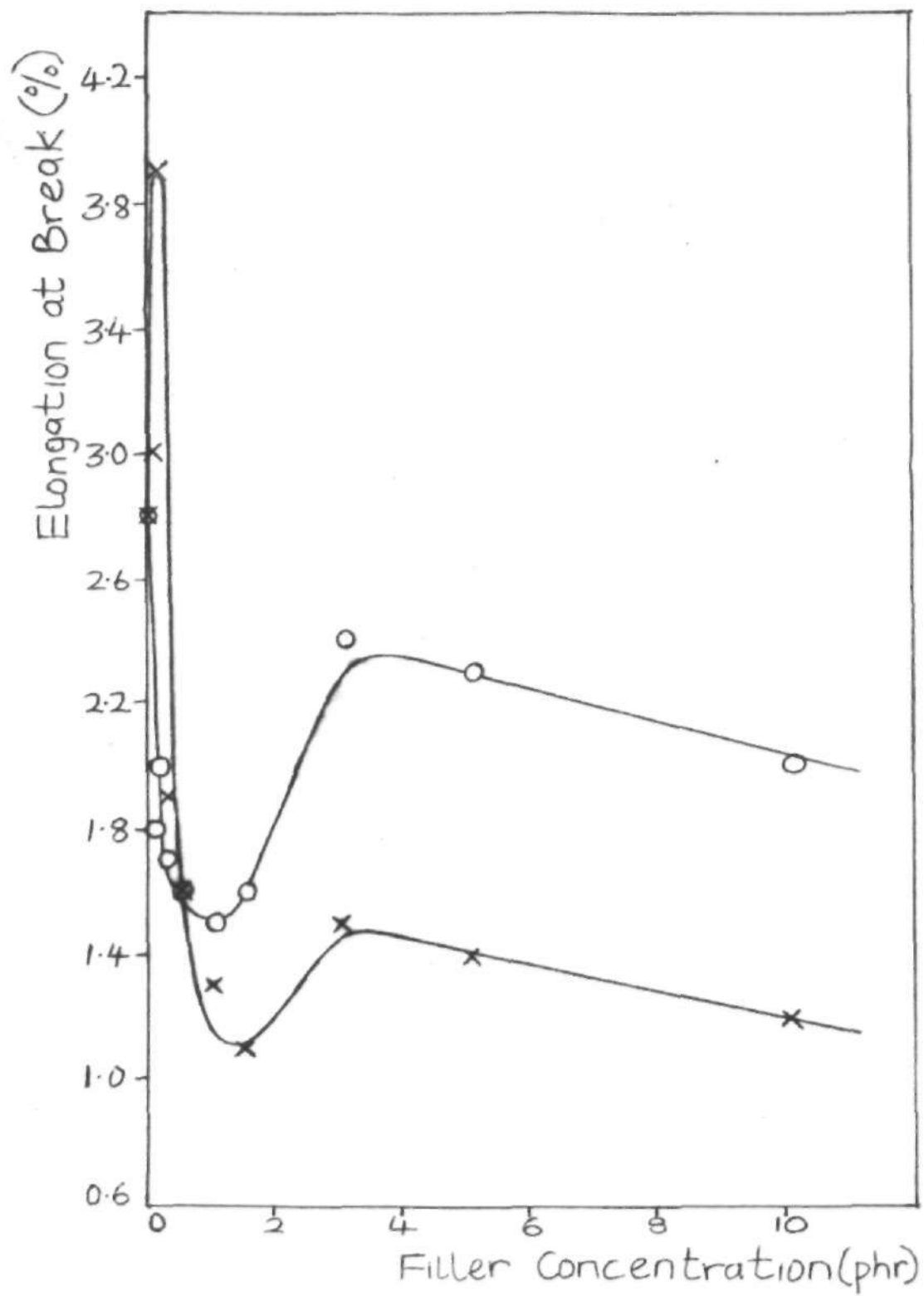


FIGURE 4.5

Variation of elongation at break
with filler concentration

x = HUC ; o = HUB

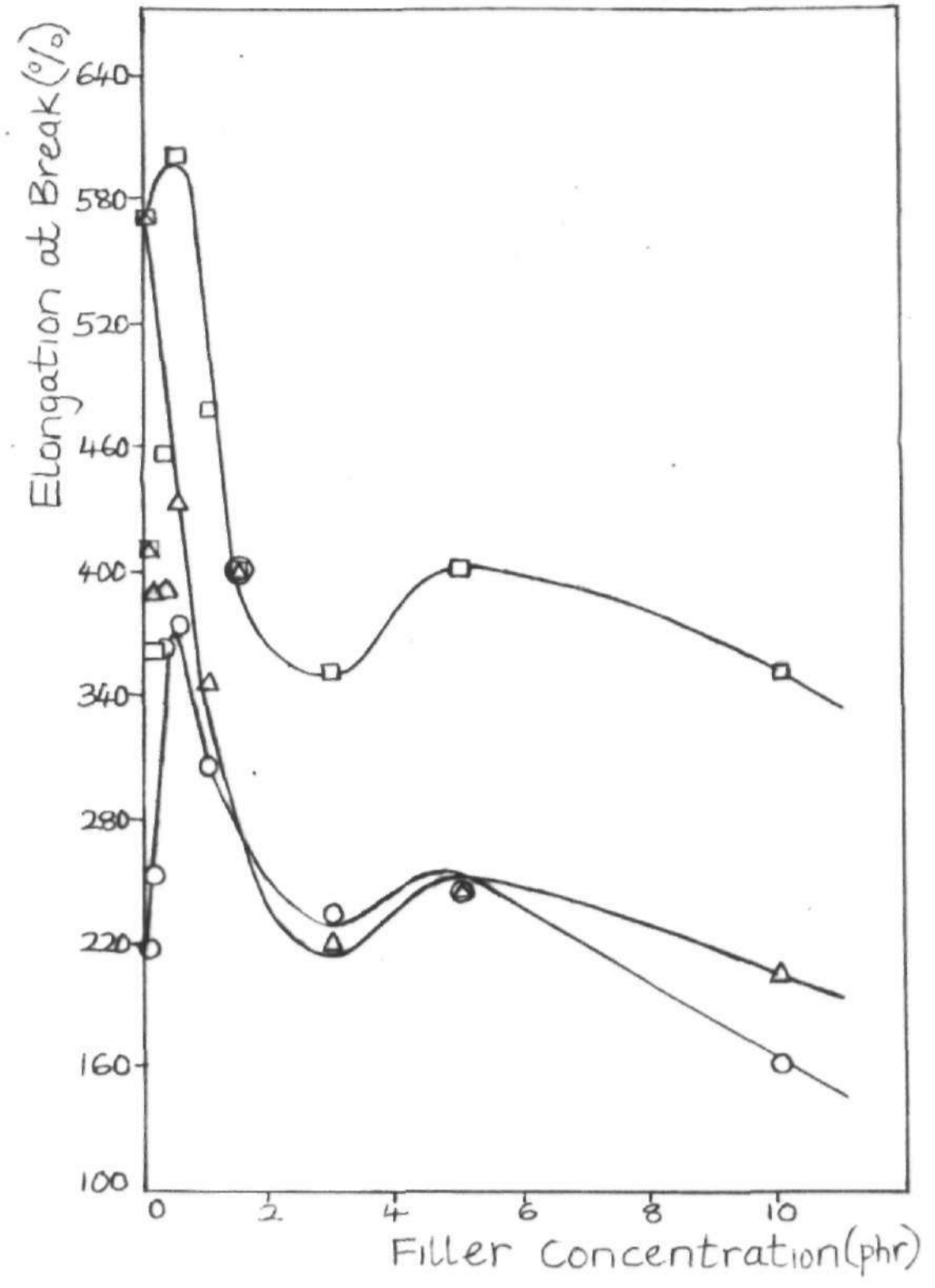


FIGURE 4.6

Variation of elongation at break with filler concentration
□ = LPC; Δ = LPB; ○ = HPB

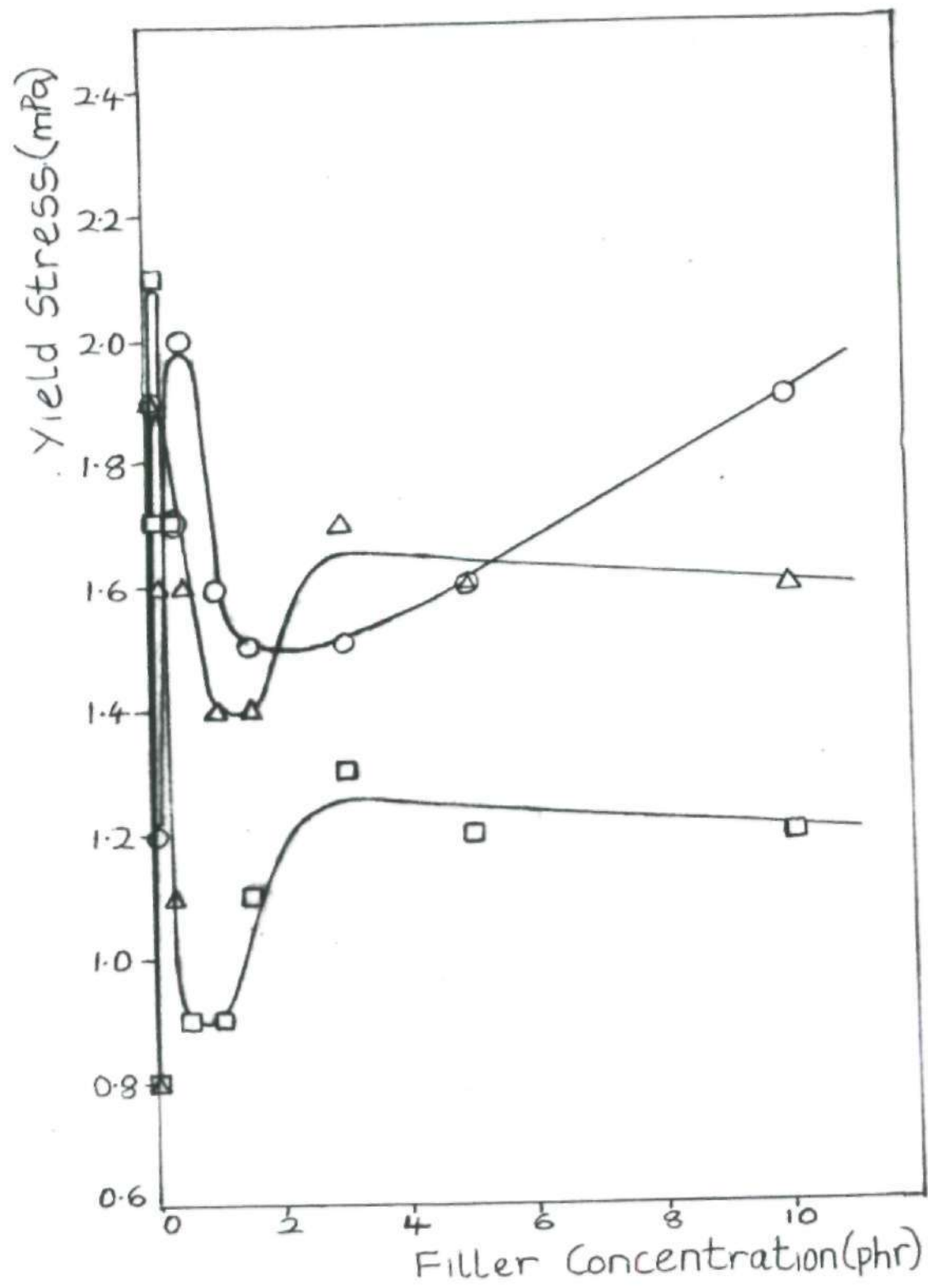


FIGURE 4.7

Variation of yield stress with filler concentration

□ = LPC; Δ = LPB; ○ = HPB

4.2 Results and Observations

4.2.1 Visual Characteristics Of Moulded Sheets.

Under visual examination, all the low-shear sheets (L-series) appear completely homogeneous. The only exception being the LUZ samples which appeared uniform only up to 3.0phr weight fraction of the filler after which granular structures were clearly visible.

Similarly, the high-shear sheets (H-series) appeared partially homogeneous with the inclusion of spots within the sheet matrices, containing regions of unfused and probably poorly mixed PVC resin and the additives.

The colour of the sheets was also examined. The LUC and LPC samples were transparent at low filler concentration but became progressively translucent and greyish with increasing filler concentration. The LUB and LPB samples were translucent and black at low filler concentration but became opaque with increased filler concentration. The LUZ sheets were first transparent, then white and translucent and finally opaque and black, indicating some level of thermal degradation.

The high-shear sheets had a tinge of brown colouration superimposed on their colours. The HUC sheets were first

transparent and then translucent and grey with increased filler concentration. The HUB and HPB sheets were black, they were first transparent, then translucent and finally opaque.

4.2.2 Tensile Properties of PVC Sheets

Three tensile properties were evaluated, these are fracture stress (FS), elongation at break (EB) and yield stress (YS). However, YS was calculated only for the plasticised samples since the unplasticised samples did not yield before fracture. Variation of the tensile properties with filler weight fraction are presented in Figures 4.1 to 4.7.

The changes follow the same trend for both the rigid and the plasticised samples. The trend also appears to be independent of the chemical nature of the filler used.

An initial increase was observed in all the figures, with the exception of Figures 4.5 and 4.6 (HUB and LPB) respectively. The increase continued to a peak, occurring between 0.05 and 1.0phr weight fraction of the filler. From the peak, there was a decrease to a minimum value, occurring between 1.0 and 1.5phr for the rigid samples (Figures 4.1, 4.2, 4.4 and 4.5) and between 1.5 and 3.0phr for the plasticised samples (Figures 4.3, 4.6 and 4.7). A minimum value was not observed in the LUZ FS plot (Figure 4.1), instead, after the peak, a rapid decrease which became gradual at

3.0phr filler concentration was observed.

After the minimum value, all the plots show an increase in the values of the tensile properties. The values level off at higher weight fractions of the filler. The LUC FS plot (Figure 4.1) and the YS plots (Figure 4.7) differ from the others in a significant respect. In the LPC and LPB YS plots and the LUC FS plot, only a marginal increase in the YS and FS values was observed after the minimum, the values remain constant above 3.0phr filler concentration. In the HPB YS plot, a continuous increase in YS values was observed, to the limit of filler concentration used, after the minimum value.

The FS plots of the unplasticised samples (Figures 4.1 and 4.2) show that the relative positioning of the different plots was not specifically influenced by filler type or mixing shear regime. In the figures, while the high-shear (HUC) plot is higher than the low-shear (LUC) plot, the high-shear (HUB) plot is lower than the low-shear (LUB) plot. Hence, no definite trend was established based on mixing shear regime in the FS plots for the rigid samples. In Figure 4.1, the plot of calcium carbonate (CC)-filled samples (LUC) is lower than that of carbon black (CB)-filled samples (LUB) but in Figure 4.2, the plot of the CC-filled samples (HUC) is higher than that of the CB-filled samples (HUB). Thus, the filler type also did not establish a definite trend in the FS plots for the unplasticised samples.

In the fracture stress plots of the plasticised samples (Figure 4.3), the plot of the CC-filled samples (LPC) is lower than that of the CB-filled samples (LPB). This establishes the trend observed in Figure 4.1 where the LUC plot was lower than the LUB plot. The trend of the high-shear samples (H-series) could not be verified since only one set of high-shear sample (HPB) was plasticised due to non-availability of materials. A more pronounced minimum was observed for the HPB samples than was observed for the LPB samples, as seen in Figure 4.3. Generally, the minima are broader for the plasticised samples than for the unplasticised ones.

The peaks in the plots of both the rigid and plasticised high-shear samples are better defined than those in the plots of the low-shear samples, as seen in their FS plots. The peak of the LUC plot (Figure 4.1) is almost non-existent.

The overall FS values of the high-shear samples are similar to those of the low-shear samples, with samples filled with the same filler having similar values. The only exception being the HUC samples whose FS values are much higher than those for the LUC samples. The FS values of the LUZ samples are also comparable with the rest but only between 0 and 3.0phr weight fraction of Zinc stearate, beyond 3.0phr, the values become very low. Also, the FS values of the unplasticised samples are generally higher than those of the plasticised samples.

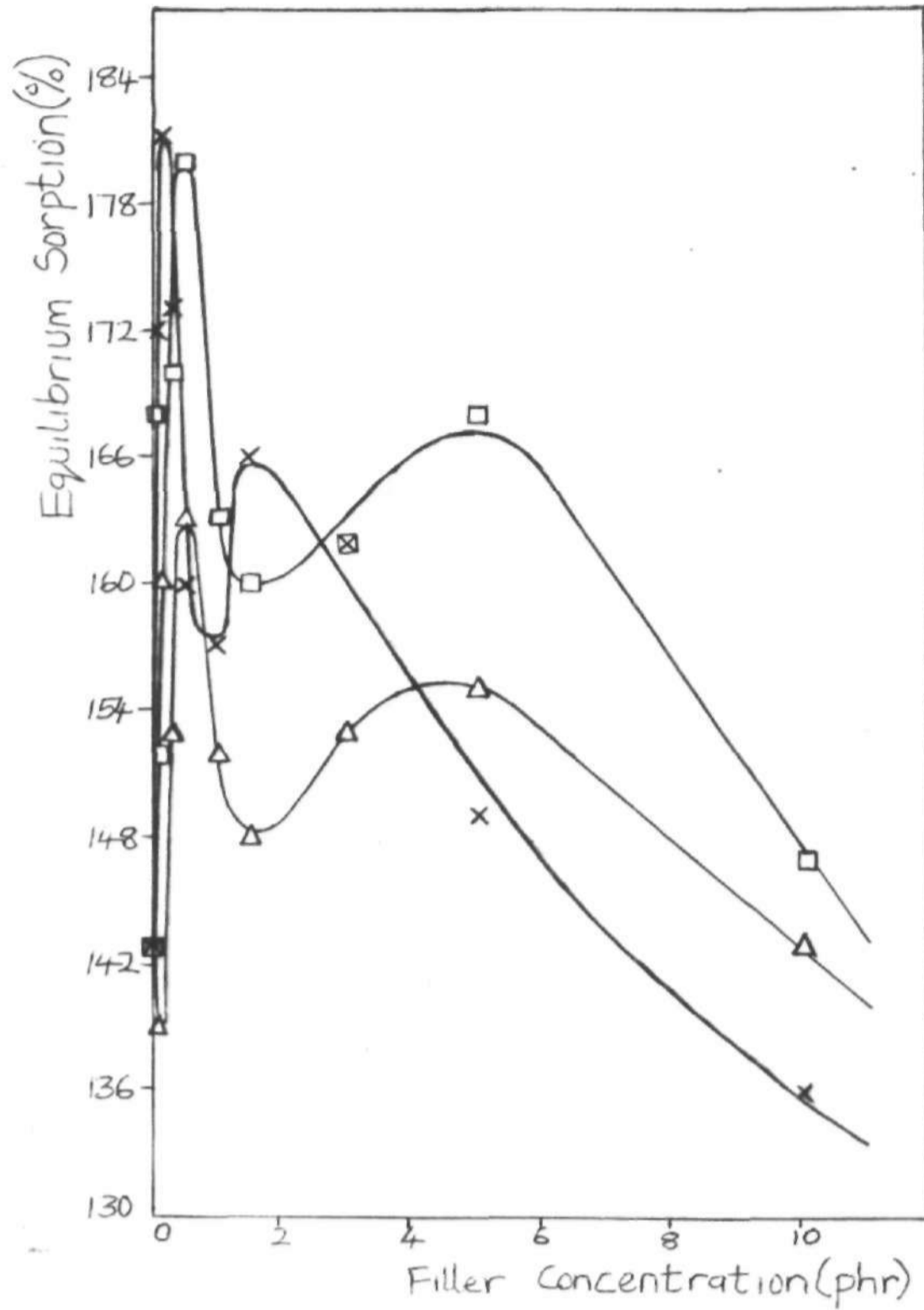


FIGURE 4.8

Variation of equilibrium sorption
with filler concentration

□ = LUC; Δ = LUB; X = LUZ

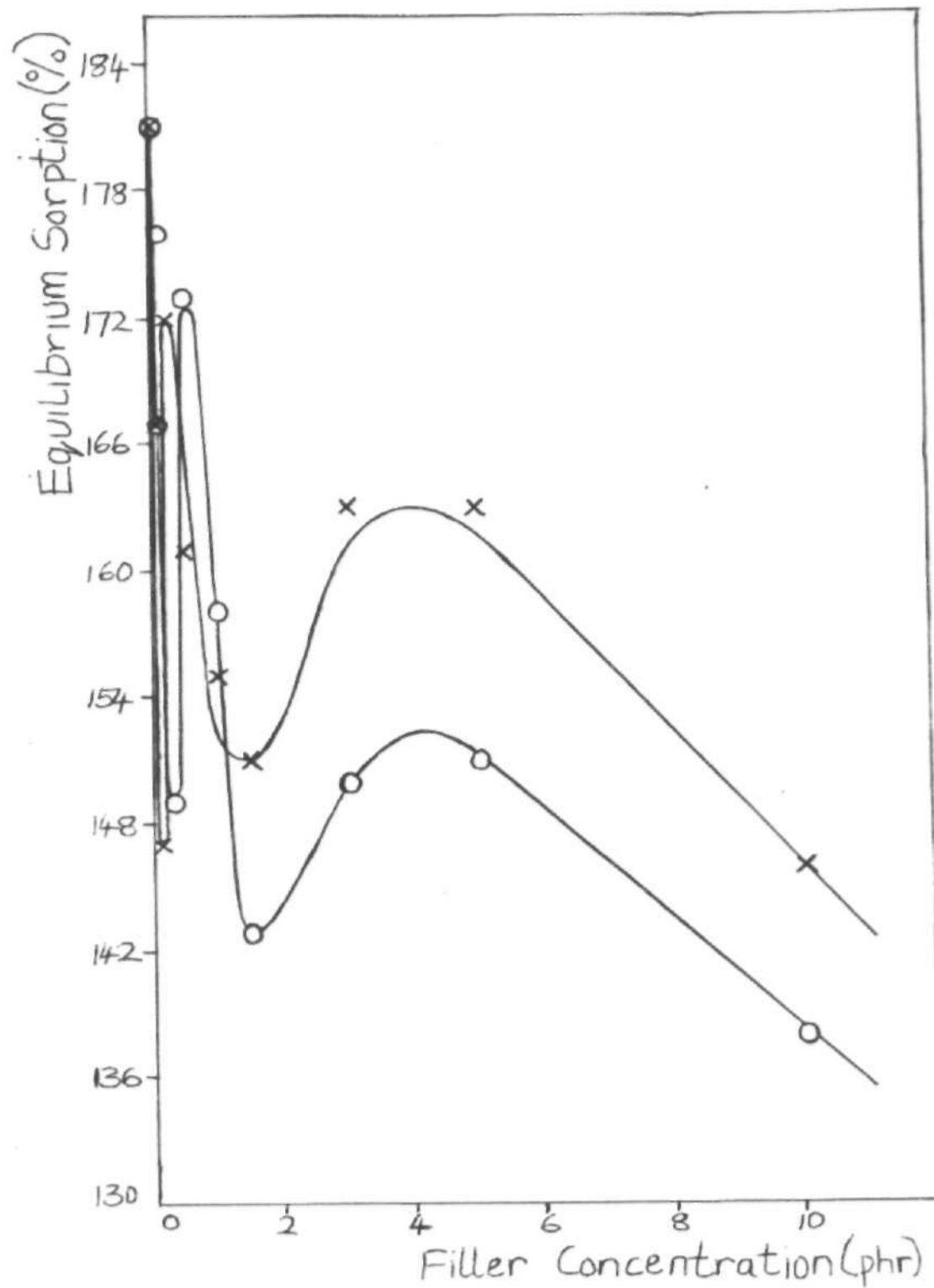


FIGURE 4.9

Variation of equilibrium sorption with filler concentration.

x = HUC; o = HUB

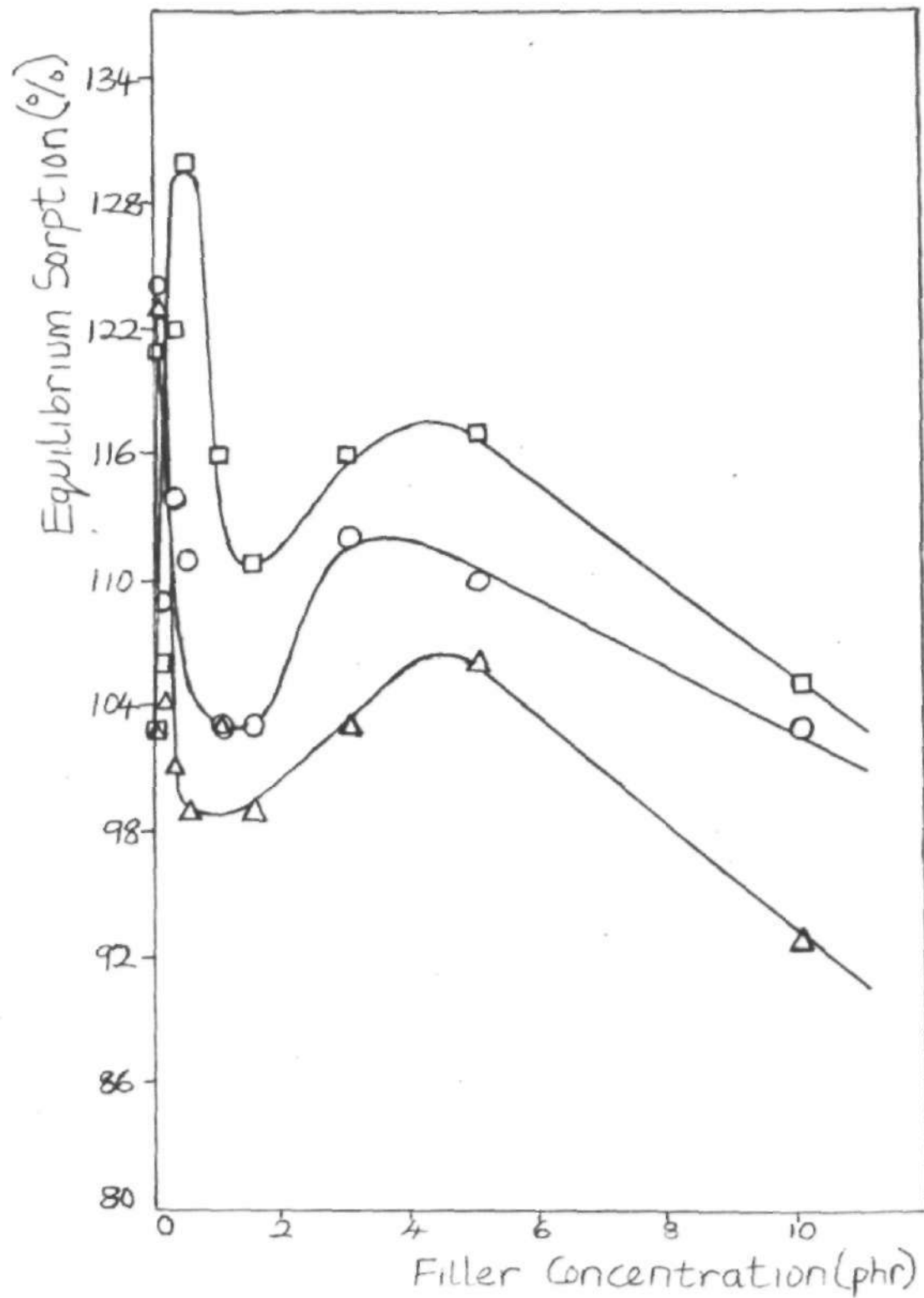


FIGURE 4-10

Variation of equilibrium sorption with filler concentration.

□ = LPC; Δ = LPB; ○ = HPB

The EB plots of the unplastified samples (Figures 4.4 and 4.5) show that both the high- and low-shear CB-filled samples are relatively higher than the CC-filled samples in the figures. And although the EB values for samples filled with the same filler are generally similar, the peak values of the high-shear samples are higher than those of the low-shear samples. Also, the EB values of the LUZ samples are comparable with the rest, but as before, only between 0 and 3.0phr filler concentration.

The elongation at break values of the plasticised samples are much higher than those of the rigid samples, with the LPC samples having much higher values than the LPB and HPB samples (Figure 4.6). This observation tallies with the one made in Figure 4.1, where the HUC samples had much higher FS values than the other samples.

In the yield stress plots (Figure 4.7), the same trend of the CB-filled samples being higher in the figure than the CC-filled samples was observed. Just as in the FS and EB plots, the values of the high- and low-shear samples are comparable.

It was also observed in all the figures (4.1 to 4.7) that generally, in the plots of the plasticised samples, the minima are not only broader than those in the plots of the rigid samples, they are also shifted to higher filler concentrations.

4.2.3 Equilibrium Sorption And Specific Gravity of the PVC Sheets

The equilibrium sorption and specific gravity of the sheets were measured to give an understanding of changes occurring in molecular order within the moulded sheets and also to verify the trends established by the tensile properties. This is possible because according to ASTM D1434-58, a correlation exists between sorption, crystallinity, density and bulk structure. Moreover, Sperati et al. (1953); Sheldon (1963); Gray and Gilbert (1976); Obande and Gilbert (1989) and Obande et al. (1993) amongst other workers have used both solvent sorption and density measurements to investigate molecular structure and estimate crystallinity of polymer samples.

Specific gravity (SG) instead of density was determined during this study. This was because the equipment for density determination was faulty at the time. Moreover, density and specific gravity are numerically equal at ambient temperatures of 4°C and below according to Whitten and Gailey (1981). They continued further that between 4° and 25°C, the differences between SG and density values are insignificant.

Hence, at 25°C and below, specific gravity and density can be assumed to be numerically equal. The specific gravity determinations carried out during this study were done between 24° and 26°C and so the values obtained thereby represent the densities of the PVC sheets.

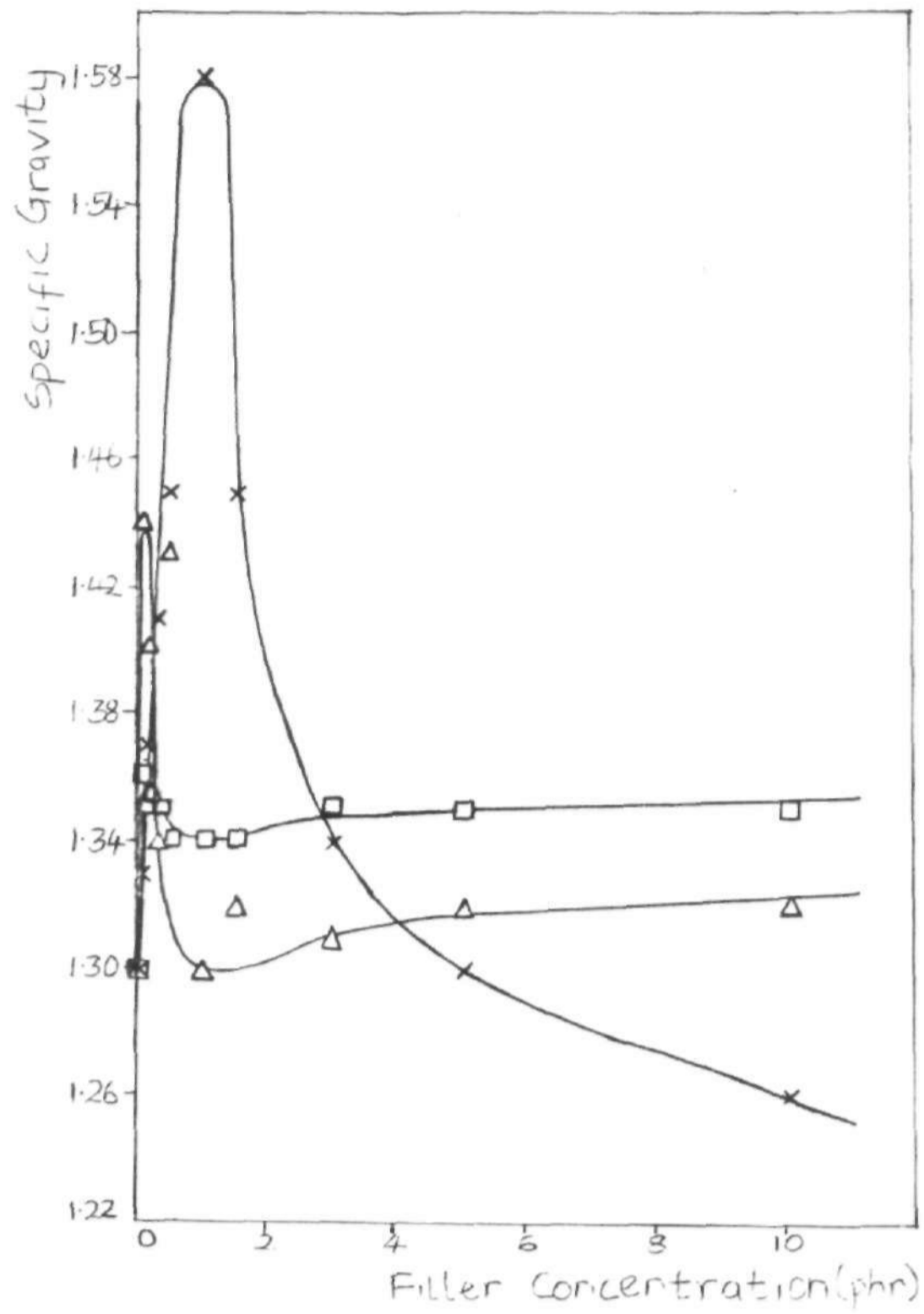


FIGURE 4-11

Variation of specific gravity
with filler concentration

□ = LUC; Δ = LUB; × = LUCZ

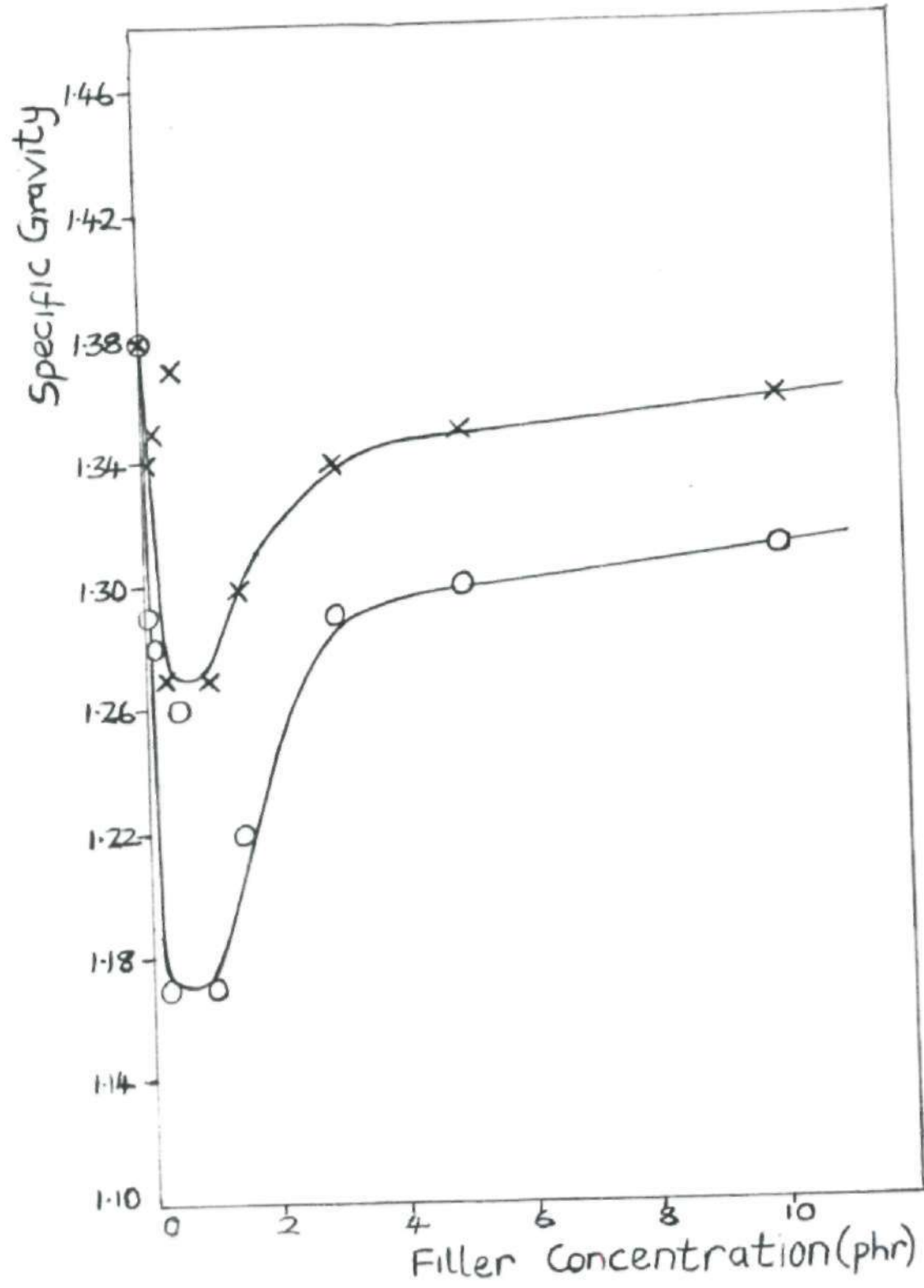


FIGURE 4.12

Variation of specific gravity
with filler concentration
x = HUC; o = HUB

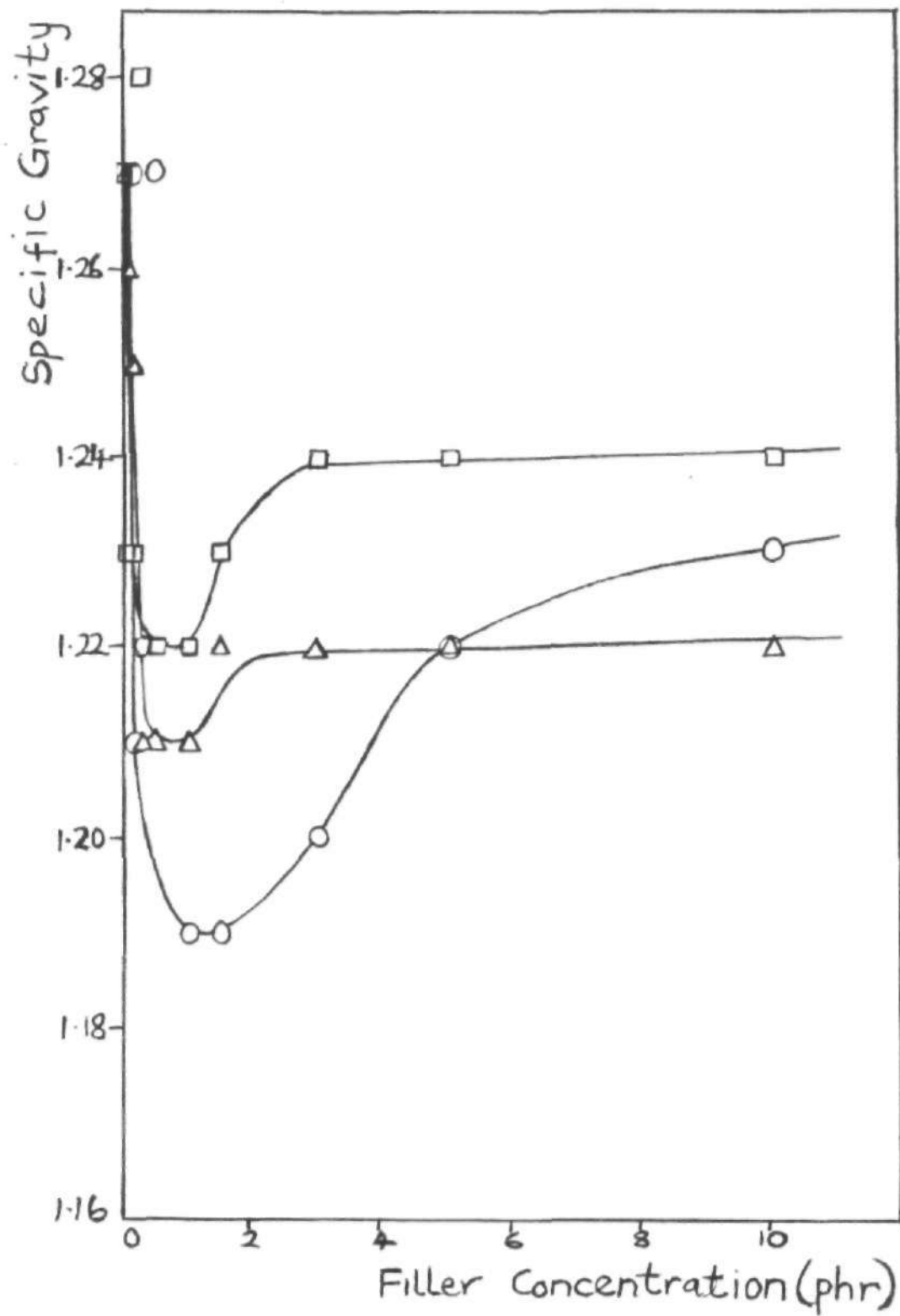


FIGURE 4.13

Variation of specific gravity
with filler concentration

□ = LPC; Δ = LPB; ○ = HPB

I Equilibrium Sorption

Variations of equilibrium sorption (ES) value with filler weight fraction are presented in Figures 4.8 to 4.10. All the plots have similar trends.

In some cases, for example, the plots for the LUB samples (Figure 4.8) and the HUC and HUB samples (Figure 4.9), a slight decrease in ES values was observed between 0.05 and 0.3phr filler concentration. This was followed by an increase which continued to a peak value between 0.1 and 0.5phr, which was observed for all the samples. After the peak, there was a decrease to a minimum, occurring between 1.0 and 2.0phr filler concentration. Thereafter, a slight increase in ES value was observed, followed by a drop to the limit of filler concentration used.

The equilibrium sorption plots show that the calcium carbonate (CC)-filled samples have higher ES values than the carbon black (CB)-filled samples. The Zinc stearate (ZS)-filled samples (LUZ) repeated the two-stage characteristic observed for the tensile properties. In the first stage, between 0 and 3.0phr weight fraction of ZS, the ES values of the LUZ samples are comparable with those of the low-shear unplastified CC-filled samples (LUC). But in the second stage, between 3.0 and 5.0phr Zinc stearate concentration, the LUZ samples had ES values similar to those of the low-shear unplastified CB-filled samples (LUB), as can be seen in

Figure 4.8.

The ES values of the high-shear samples (Figure 4.9) are a maximum for zero filler concentration but those of the low-shear samples (Figure 4.8) are minimum at the same point. But with the incorporation of low weight fractions of filler into the PVC matrix, the ES values of the low-shear samples increased rapidly to a peak value, while those of the high-shear samples decreased slightly and then increased to a peak value.

The peak values are comparable for all the unplasticised samples (Figures 4.8 and 4.9), with the exception of that of the LUB samples (Figure 4.8) which is slightly lower than rest. The peak values of the plasticised samples (Figure 4.10) are also similar but that of the low-shear CC-filled samples (LPC) is a bit higher than the others.

After the peak, with increasing weight fraction of the filler, the ES values for both the high- and low-shear sheets become comparable, with samples filled with the same filler having similar values.

II Specific Gravity

Variations of specific gravity (SG) value with filler concentration are shown in Figures 4.11 to 4.13. All the plots, with the exception of that for the Zinc stearate-filled (LUZ) samples (Figure 4.11), show a similar trend, with only

slight differences.

In some of the plots, like those for the LUC and LUB (Figure 4.11), a sharp increase in SG value is observed to occur at 0.05phr filler concentration. This is followed by a decrease which continued to a minimum value, occurring between 0.5 and 2.0phr for all the samples.

For the low-shear sheets (Figures 4.11 and 4.13), after the minimum, the SG value increased slightly and then became constant with increasing weight fraction of the filler. For the high-shear sheets, the SG values increased rapidly after the minimum. The rapid increase continued to 3.0phr filler concentration for the rigid and 5.0phr for the plasticised samples, the decrease become gradual thereafter.

The Zinc stearate (ZS) filled samples (LUZ) behaved rather differently from the other samples. For the LUZ samples (Figure 4.11), an initial increase in SG values which continued to a peak value at 1.0phr filler concentration, was observed. Thereafter, a rapid decrease was noted upto 3.0phr after which the decrease became gradual.

The trend established by the filler types in the SG plots agrees with what was observed in the equilibrium sorption plots. The calcium carbonate (CC)-filled samples had higher SG values than the carbon black (CB)-filled samples. The ZS-filled samples (LUZ) had relatively high SG values, comparable

with those of the low-shear CC-filled samples (LUC) in the region of filler concentration 0 to 0.1 and 2.5 to 3.5phr. Between 0.1 and 2.5phr, the SG values of the LUZ samples are much higher. But between 3.5 and 6.0phr, the LUZ SG values are similar to those of the low-shear CB-filled (LUB) samples (Figure 4.11).

The SG values of both the high-shear and the plasticised samples are a maximum for zero weight fraction of the filler but those of the low-shear samples were minimum at the same point. However, at the incorporation of very low weight fractions of the filler into the PVC matrix, the values of the low-shear sheets increased sharply to a peak value, the high-shear samples only experienced a slight decrease in SG values at a similar weight fraction of the filler.

With increasing weight fractions of the filler, all the samples with the exception of the LUZ samples, experience a decrease in SG values until the minimum is reached. The minimum is broader for the low-shear unplasticised samples (Figure 4.11) and the high-shear plasticised samples (Figure 4.13) than for the low-shear plasticised (Figure 4.13) and the high-shear unplasticised (Figure 4.12) samples. The minimum also, is deeper for the high-shear samples than for their low-shear counterparts (compare Figure 4.11 with Figure 4.12 and 4.13) and the SG value of the high-shear samples at this point, are much lower than those of the low-shear samples

From the minimum value, the rapid increase in the SG value of the high-shear samples continued to between 3.0 and 5.0phr filler concentration. Now, the SG values of the high-shear samples are comparable with those of their low-shear counterparts. From this point, the increase in the SG values of the high-shear samples was marginal.

However, for the low-shear samples, the increase in SG value after the minimum value was very marginal and the values became constant between 3.0 and 5.0phr filler concentration. Thereafter, there was no further change in the SG value of the low-shear samples up to the limit of filler concentration used.

Between 3.0 and 10.0phr filler concentration, the SG values for both the high- and low-shear calcium carbonate- and carbon black-filled samples are similar. This is true for both the rigid and the plasticised samples but the range of filler concentration for the plasticised is 5.0 to 10.0phr.

4.3 DISCUSSIONS

4.3.1 Effect of Formulation Components and Processing Parameters on the PVC Sheets - Deductions From Visual Characteristics

Visual examination of the moulded PVC sheets showed a slight discolouration and the presence of spots within the high-shear sheets. Also, a lack of fusion was observed with

some of the LUZ samples. Apart from these flaws, the sheets were generally alright.

The slight discolouration which showed off as a tinge of brown in the colour of the high-shear sheets may be due to the type of stabiliser used in the high-shear formulations. Two variations of dibasic lead stearate (DBLS I and II) were used for stabilisation in the high-shear samples

DBLS I being a finely powdered solid was effectively mixed with the PVC resin but DBLS II, which was in form of precompounded rod-like pellets did not result in a homogeneous mixture with the PVC resin due to its particulate nature. The DBLS II pellets were not completely comminuted to powder because the mixing did not involve high temperatures. The temperatures generated during the high-shear mixing were not high because the rotors and chamber walls were not heated during the mixing due to unavoidable technical faults.

According to Smuckler and Finnerty (1974), the finer the particle size of an additive the more effective the additive because of the increased interfacial area between the additive and the base polymer. Thus, the effectiveness of DBLS II was low due to its particulate nature which reduced its surface area available for interaction with the polymer. The size of the DBLS II pellets could have been reduced to a fine scale if higher temperatures were generated during mixing. Also, if the rotor design was different such that the rotors could

effectively reach all parts of the mixing chamber, DBLS II could have been more uniformly mixed and therefore would have performed better.

The spots observed with the high-shear sheets may also be due to the rotor design of the Banbury mixer. Similar spots have been observed by Carleton and Mishuck (1964) and Boulton (1973) in PVC articles processed from dry blends. They referred to these spots as "fish-eyes". But while Carleton and Mishuck (1964) explain that the spots are due to uneven distribution of additives within the PVC matrix, Boulton (1973) reports that the spots are highly sheared parts of the formulations. He explains further that, the highly sheared parts are areas where the rotors sweep the walls of the mixing chamber.

The spots were much fewer with the plasticised samples than with the unplasticised samples. The addition of a plasticiser changed the formulation from a dry blend to a putty mixture, in this form, the rotors are better able to pull all parts of the formulation into the mixing zone. This way, the additives are evenly distributed within the PVC matrix and all parts of the formulation get equally sheared. This explains the reduction of the spots in the plasticised samples.

The lack of fusion observed with some of the LUZ samples which resulted in the appearance of granular structures may be

due to the type of filler used in these samples. In the LUZ formulations, PVC was filled with Zinc stearate. Zinc stearate is a metallic soap that can function both as a lubricant and as a filler, Rose (1961), and hence it is referred to as a lubricating filler. So Zinc stearate not only fills the PVC matrix, it also lubricates it. But according to Collins (1977), lubricants decrease the rate of fusion of polymer samples consequently, at above 3.0phr weight fraction of Zinc stearate, the PVC system gets over lubricated and the level of fusion of the samples decreases accordingly.

4.3.2 Influence of Mixing Shear Regime on the Tensile Properties

The PVC sheets used for the analysis were compression moulded. And since compression moulding involves little shearing of the sample, Obande (1984), the PVC grains are substantially preserved. But prior to the moulding of the sheets, the different formulations were first compounded using two types of mixers. One type, the Warring blender, involved very little shearing of the sample while the other type, the Banbury mixer, involved much shearing of the sample, Allsopp (1983)

According to Irving and Saxton (1967), the high-shear mixing operates by drawing out the components of the formulation mixture into thinner and thinner layers, on the other hand, the low-shear mixing is achieved by high speed

distribution of the additives within the polymer matrix, Boulton (1973).

It can be seen from the values of the tensile properties (Figures 4.1 to 4.5) that the high-shear samples had more pronounced peaks than the low-shear samples. This feature was more prominent with the rigid than with the plasticised samples. However, no peak was observed for the HUB (Figure 4.5) and LPB (Figure 4.6) samples. In the HUB and LPB plots, the value of the measured parameter was maximum at zero filler concentration.

The well-pronounced peaks for the high-shear samples may be due to differences in the two types of mixing actions. The high-shear mixing by virtue of the continuous drawing of the mixture components into thinner and thinner sections, will enhance orientation within the samples. And as has been noted by Elias (1977), the enhanced orientation will cause a change in mechanical properties. Hence, the higher orientation obtainable in the peak areas increases the initial fracture toughness of the high-shear samples. The low-shear mixing did not give rise to a similar orientation, as a result, a high initial fracture toughness is lacking in the low-shear samples.

Between the peak and the minimum values, there were no noticeable differences between the high- and the low-shear samples. However, beyond the minimum, some differences were

observed in the yield stress (YS) value of the high- and low-shear samples. After the minimum, the YS values of the low-shear samples showed only a marginal increase, after which the values level off. While the YS values of the high-shear samples increased continuously up to the limit of filler concentration used (Figure 4.7).

The continuous increase in YS values may also be traced to the enhanced orientation in the high-shear samples. According to Mailabari (1988), the structure of the PVC blend, beyond the minimum, consists of integral composites of coherent aggregates of PVC grains and those of filler particles. The aggregates become highly oriented and this results in the improvement of mechanical properties proposed by Elias (1977). In the low-shear samples, since the PVC grain aggregates and those of the filler particles are not highly oriented, only a marginal increase is observed in the YS values of these samples.

Apart from the differences in the peak values and those in the YS values beyond the minimum, the values of the tensile properties are similar for both the low- and high-shear samples generally.

In most of the figures, the CB-filled samples are higher than the CC-filled samples, indicating higher values of the tensile properties for the former. The trend was, however, broken for the HUC (Figure 4.2) and LPC (Figure 4.6) samples

with HUC being higher than HUB and LPC, higher than LPB samples. Both the HUC and LPC samples were calcium carbonate-filled, the difference between them being that, while the former is high-sheared and unplasticised, the latter is low-sheared and plasticised. For the same effect to be observed in the two sets of samples, it should follow that both a high mixing shear regime and plasticisation probably, have similar effects on calcium carbonate-filled samples, this will have to be properly verified. It then appears that plasticisation may have resulted in an increase in the shear intensity, and hence in orientation within the low-shear calcium carbonate-filled samples (LPC) to make them similar to the high-shear calcium carbonate-filled unplasticised samples (HUC).

4.3.3 Effect of Plasticisation on the Tensile Properties

The tensile properties under consideration here, are fracture stress (FS) and elongation at break (EB). Yield stress (YS) is not considered since YS values were obtained only for the plasticised samples. There will therefore be no basis for the evaluation of the effect of plasticisation on the YS values.

The plasticised samples had lower FS values than those of the rigid samples (compare Figures 4.1 and 4.2 with Figure 4.3). This may be due to a reduction of the aggregation of the polymer molecules brought about by plasticisation. Paton

(1972) has shown that plasticisation reduces aggregation. This effect reduces the fracture strength of the samples, such that the FS values of the plasticised samples are then lower than those of their corresponding rigid samples.

As is typical with plasticiser effects, the EB values of the plasticised sheets are much higher than those of the rigid sheets (compare Figure 4.6 with Figures 4.4 and 4.5). This, of course, is due to the well known increase in flexibility and elongation brought about by plasticisation, Gould (1965). This effect increases the gelation of the sheets such that the polymer becomes ductile. The resultant effect of the above is a rise in the EB values of the plasticised sheets.

Apart from the reduction in FS values and the increase in EB values, it appears that plasticisation enhanced initial orientation in the low-shear samples, such that the peaks of both the low- and high-shear plasticised samples are similar (compare Figures 4.1 and 4.2 with Figure 4.3) and also (Figures 4.4 and 4.5 with Figure 4.6). The above effect can even be seen in the YS plots (Figure 4.7) of the LPC, LPB and HPB samples.

By transforming the different formulations from free-flowing blends into putty mixtures, plasticisation may have resulted in an increased shear intensity within the samples. This may have, in turn promoted higher orientation within the low-shear plasticised samples, increasing the peak values in

the process. It may then be suggested that plasticisation, somehow, reduced the differences between the low- and high-shear samples.

4.3.4 Influence of Filler Type on the Tensile Properties

Fillers can be classified in a number of ways, one of these, is the classification according to specific function in polymers. On this basis, fillers can be reinforcing, lubricating, bulking or cheapening, King (1972). Some fillers combine two or more of the above functions while others are used to improve general properties.

The three types of fillers used in this study are calcium carbonte (CC), carbon black (CB) and Zinc stearate (ZS). CC is traditionally classified as a bulking or cheapening filler.

CB is classified as a reinforcing filler and ZS as a lubricating filler.

The results of the tensile tests show that the plots of the CB-filled samples were relatively higher in the figures, than those of the CC-filled samples. The implications are that the CB-filled samples had higher fracture stress (FS), elongation at break (EB) and yield stress (YS) values than the CC-filled samples. CB may then be said to have enhanced the tensile properties of the PVC samples to a greater extent than CC, this is not unexpected since CB is a reinforcing filler.

The plots of the ZS-filled samples are similar to those of the low-shear CC- and CB-filled samples. Between 0 to 1.0phr, the ZS plots are similar to the CB plots but between 1.0 - 3.0phr, they are similar to the CC plots.

The HUC samples (Figure 4.2) and the LPC samples (Figure 4.6) differ from the others in a significant respect. For these samples, which are calcium carbonate-filled, the general trend of carbon black-filled samples having higher values of the tensile properties than their calcium carbonate-filled counterparts was not observed.

For any filler to improve the tensile properties of a polymer, that filler should be able to interact intimately with the polymer chains and hence alter the supermolecular structure of the polymer. This intimate interaction between filler and polymer is what causes the enhancement of tensile and other mechanical properties. It follows then that CB had a more intimate interaction with the polymer chains than CC.

Zinc stearate, as stated before, is a lubricating filler, this is why beyond 3.0phr, granular structures are observable with the samples, the system being overlubricated then. Overlubrication gives rise to low frictional heat and excessive interparticle slippage which results in a rapid drop in fusion level, Mascia (1974).

The presence of Zinc stearate in the grain boundaries of

PVC prevents the destruction of its primary crystallites due to the increased lubricity of the formulation. This increased lubricity enhances crystallinity since the chains then have sufficient mobility and can orient themselves to favour crystallinity. This effect continues until the weight fraction of the filler is high enough to cause a reduction in the rate of fusion. When this happens, crystallinity and fusion decrease because of overlubrication. This explains the two stage characteristic of the tensile properties of the Zinc stearate-filled samples.

Calcium carbonate is a bulking filler and so does not interact much with the polymer chains. But the high mixing shear regime seems to have increased the interaction between the filler particles and the polymer chains such that the tensile properties of the high-shear unplasticised calcium carbonate-filled samples (HUC) are much better than those of their low-shear counterparts (LUC).

The increased values of the tensile properties of the low-shear plasticised calcium carbonate-filled samples (LPC) is consistent with the above, since plasticisation was observed earlier on to have resulted in an increase in shear intensity during mixing.

4.3.5 Changes in Molecular Order of the PVC Sheets - Deductions from Sorption and Specific Gravity Results

PVC is one of the semi-crystalline polymers which have been reported to contain microvoids. These voids are introduced into the polymer structure during crystallization, Matsuoka (1961) and, Machin and Rogers (1970). Matsuoka (1961) explains that the voids are domains of zero density and as such, a high density polymer will have a low population of voids. Also, expectedly, and as has been shown by Machin and Rogers (1970), the overall sorptive capacity of polymers with inherent voids will naturally be influenced by the presence of these voids.

Furthermore, Obande et al. (1993) have recently reported that, apart from the inherent voids in PVC, that the incorporation of filler particles into the polymer matrix causes alterations in the molecular order of the polymer. They proposed a four-stage mechanism to account for these changes.

They explained that the stages consist of a thin dispersion of the filler at low concentration; lubrication of the polymer particles at sufficient filler volume fraction; saturation of the gaps between polymer particles by the filler; and the formation of distinct phases of clusters of additive and polymer particles. All four stages have specific effects on the bulk phase structure and hence on the product

property.

As stated before, the processing method used to prepare the sheets, that is, compression moulding was not shear intensive and so it left the molecular order of the samples almost intact. But the mixing of the additives with the PVC resin, especially the high-shear mixing, affected the polymer bulk structure and hence the molecular order within the samples.

So, in estimating the changes in molecular order of the polymer with increasing weight fraction of the filler, the effect of mixing shear regime on the ordered arrangement can also be evaluated.

The equilibrium sorption (ES) and specific gravity (SG) results can be interpreted on the basis of the four-stage action proposed by Obande et al. (1993), also the effect of mixing shear regime on the results can be explained alongside.

The first stage, according to the proposed mechanism is the dispersion stage. The additive is thinly dispersed within the gelled network between polymer particles. An "exclusion zone" or void is formed around each filler particle, this helps to arrest the growth of an advancing crack and results in an initial fracture toughening of the polymer.

In the ES plots (Figures 4.8 to 4.10), the dispersion stage is observed as a peak. The incorporation of the filler

particles increases the level of disorder within the polymer matrix and since sorption takes place in the disordered regions, Obande and Gilbert (1989), ES values will also increase.

In the SG plots (Figures 4.11 - 4.13), the dispersion stage is observed as a decrease to a minimum. This should be due to the decrease observed in the level of order within the polymer, density decreases here, since it is a measure of the level of order within the polymer.

Prior to the dispersion stage, a drop in ES value and a corresponding increase in SG value is observed at 0.05phr for some of the samples like LUB (Figure 4.8), HUC and HUB (Figure 4.9) and, LUC and LUB (Figure 4.11). This stage may be due to the filling of the inherent voids in the polymer by the filler particles which consolidates the polymer matrix, causing a decrease in sorption and an increase in specific gravity values. This stage was not accounted for in the proposed mechanism.

Both the low- and high-shear samples highlighted the first stage of the mechanism. But while the high-shear unplastified samples (Figure 4.9) all showed the initial stage in the ES plots, only one of the low-shear unplastified samples, the LUB (Figure 4.8) did. On the contrary, only the low-shear unplastified LUC and LUB (Figure 4.11) samples highlighted the initial stage in the SG plots, the other

samples did not.

The second stage in the mechanism is the lubrication stage, here the filler concentration is high enough to lubricate the PVC particles, by forming a thin coating around each particle. This process is thought to relieve inter-PVC grain friction.

In the ES plots, the lubrication stage is seen as a decrease from the peak to a minimum value. The higher concentration of the filler used here, causes the filler particles to lubricate the PVC grains such that the "exclusion zones" around the former are eliminated. This reduces the level of disorder within the polymer matrix and hence the drop in ES values.

In the SG plots, the lubrication stage corresponds to a marginal increase in SG value for the low-shear samples (Figures 4.11 and 4.13). This stage marks a considerable increase in SG values for the high-shear samples (Figures 4.12 and 4.13). This tallies with the proposed increase in the level of orderedness at molecular levels. Density should increase with a corresponding increase in level of order.

In the high-shear plots (Figure 4.12), the increase experienced in the SG value at this stage, is much higher than the one in the low-shear plots (Figure 4.11). This may be due to the fact that the minimum SG value of the high-shear sheets

are much lower than those of their low-shear counterparts.

The minimum ES value of both the low- and high-shear sheets are comparable but that of the LUZ samples (Figure 4.8) is very narrow, this may be due to the chemical nature of Zinc stearate which was the filler used in these samples.

The third stage in the mechanism is the saturation stage, the filler particles saturate the gap between the PVC grains in the melt. This process is thought to assist inter-grain friction, thereby increasing the level of gelled network of the polymer and causing an increase in fracture toughness.

In the ES plots, the saturation stage is observed as an increase from the minimum to a broad maximum value which is lower than the peak value. The filler concentration is now high enough for the filler particles to form sizeable pockets which are capable of separating weakly linked PVC grains. This results in an increase in ES value since the formation of the pockets of filler particles will somehow increase the level of disorder within the polymer matrix.

The broad maximum is comparable for both the high- and low-shear samples in the ES plots and it occurs between 3.0 and 7.0phr filler concentration for all the samples except the LUZ (Figure 4.8). For the LUZ samples, the broad maximum was observed between 1.5 and 3.0phr.

In the SG plots, the saturation stage corresponds to a

levelling off of SG value. In the plots of the high-shear samples (Figure 4.12), there is a marginal increase in SG value but the values remain substantially constant in the plots of the low-shear samples (Figure 4.11). The marginal increase in the SG value of the high-shear sheets may have occurred so that the values will be comparable with those of the low-shear sheets.

The fourth stage of the mechanism is the phase separation stage, the filler concentration is now high enough for the filler particles to form large pockets and these pockets separate similar pockets of PVC grains. The sample at this stage is weak and brittle.

In the ES plots, the phase separation stage is observed as a decrease from the broad maximum to the limit of filler concentration used for the study. This final drop in ES value may be due to the close packing of the pockets within the polymer matrix and also due to the high volume fraction of the filler as explained by Mailabari (1988).

The phase separation stage is similar for both the high- and low-shear samples in the ES plots. The ES value drop to values lower than the minimum value observed in the lubrication stage. The drop in the ES value of the LUZ samples (Figure 4.8) is substantial and is much lower than what is observed for the other samples. However, the HPB samples (Figure 4.10) are an exception, in that, their ES

value at 10.0phr, which is the highest filler weight fraction used, corresponds to the minimum value.

In the SG plots for the low-shear samples (Figures 4.11 and 4.13), the phase separation stage is not really seen since the SG values remain substantially constant, from the saturation stage. The phase-separation stage shows off in the SG plots for the high-shear samples (Figures 4.12 and 4.13) as a marginal increase in SG value. This increase in SG value of the high-shear sheets is probably because of the orientation brought about by the high mixing shear regime. This orientation appears to increase the level of order in the polymer matrix.

The LUZ SG plot (Figure 4.11) did not follow the mechanism described above. Instead, the SG value increase rapidly to a very high peak value at 1.0phr filler concentration and then decrease to the limit of filler concentration used. The peak at 1.0phr corresponds to the minimum at a similar filler concentration in the ES plot for the LUZ samples (Figure 4.8). The drop in SG value also corresponds to an increase observed in ES value beyond the minimum value.

The peak SG value for the LUZ samples is very high and is much higher than those of the other samples. At 1.0phr filler concentration where the peak is observed, the lubricity of the polymer system brought about by the filler, is high

enough to give the polymer chains sufficient mobility for them to orient themselves to favour crystallinity. And since crystallinity and density are both a measure of molecular order, Obande (1984), it follows then that an increase in crystallinity will be accompanied by an increase in density.

The drop in SG value from the peak was rapid up to 3.0phr filler concentration, thereafter, it became gradual. This gradual drop in SG value corresponds to a rapid drop also in ES value of the LUZ samples. The reason for this anomaly is not clear since density and sorption are supposed to be inversely related. It may however, be due to the poorly fused state of the LUZ samples at filler concentrations beyond 3.0phr.

CHAPTER 5

SUMMARY AND CONCLUSION

The experimental results, observations and discussions permit some conclusions to be drawn about the formulations, the effects of processing and of the different fillers on the tensile properties of the compression moulded PVC sheets.

5.1 Formulations

The formulations used for this research work are generally recommendable with the exception of some LUZ formulations. Despite the occurrence of "fish eyes", most of the high shear formulations are still recommendable and the flaws could have been avoidable if the processing conditions were different.

If DBLS II is to be used as a stabiliser in any formulations, the formulation should be compounded with a mixer type that utilizes both high levels of shear and high temperatures for its mixing action so that the stabilizer pellets will be comminuted to a fine powder scale or indeed melted. The Banbury mixer may be used in such a situation but the rotors and the walls of the mixing chamber must be heated.

However, the Banbury mixer should be used with extra care when compounding free-flowing powdery formulations because of

the rotor design of the mixer. Indeed for best results, such formulations should be plasticised.

From the LUZ formulations, it can be concluded that zinc stearate should not be used at concentration exceeding 3.0phr **if** high levels of fusion, crystallinity and fracture toughness are desired in the final product. This is because beyond 3.0phr, the PVC-filler system appears to be overlubricated and this results in the appearance of granular structures in the samples. It may also be concluded that in order to avoid overlubrication, the use of additional lubricants in zinc stearate-filled PVC systems be discouraged since the filler itself appears to be an efficient lubricant.

5.2 Effect of Processing on the Tensile Properties

Mixing shear regime was the only variable processing parameter in the preparation of the samples, hence the effect of processing will basically be the same with the effect of mixing shear regime in this context.

A high mixing shear regime was observed to enhance the tensile properties of the sheets at the incorporation of low weight fractions of the filler. This enhancement of tensile properties was attributed to the proposed increased orientation within the high-shear samples. Hence, if initial enhancement in tensile properties is desired in PVC articles,

their formulations should be compounded with a high-shear mixer.

However, for the unplasticised calcium carbonate-filled PVC systems, a high mixing shear regime improved the tensile properties throughout the range of filler concentration examined. Thus, if better tensile properties are envisaged in calcium carbonate-filled UPVC articles, the formulations should be compounded with a high-shear mixer.

5.3 Effects of Additives

The effects of additives will be summarized in three sections below:-

5.3.1 Mechanism of Filler Action and Changes in Molecular Order of the Samples

The fillers caused alterations in the molecular order of the samples. These alterations followed the four-stage mechanism proposed by Obande *et al.* (1993). But before the first stage, an initial stage which was not accounted for by the proposed mechanism was noted. The initial stage could not be verified with the aid of microscopy due to non-availability of the equipment. Notwithstanding, this stage was observed to correspond to a decrease in sorption and an increase in density due to the filling of the inherent voids in the polymer matrix by the filler particles at very low weight

fractions of the filler. This observation was made with the aid of solvent sorption and density measurements which are indirect methods.

The first stage of the proposed mechanism involved a thin dispersion of very low weight fractions of the filler within the polymer matrix, this led to the formation of an "exclusion zone" around each filler particle. The "exclusion zones" helped to terminate the growth of advancing cracks, causing the observed initial fracture toughening of the samples. The second stage was the decrease in fracture toughness which was caused by higher weight fractions of the filler within the polymer matrix, the filler particles were said to lubricate the polymer particles. The third stage resulted in the observed increase in fracture toughness of the samples which according to the mechanism is caused by increased concentration of the filler, at this point, the filler was said to saturate the gaps between the PVC grains and also assist inter-grain friction. The fourth, that is, final stage was a phase separation, between the filler particles and the PVC grains, due to higher weight fraction of the filler, here, the samples were found to be weak and brittle.

5.3.2 Effectiveness of the Filler Types

The fillers, calcium carbonate, carbon black and zinc stearate enhanced the tensile properties of the sheets. This

enhancement was most prominent at weight fractions below 1.0phr. Between 1.0 and 1.5phr, the enhancement was greatly reduced but was increased slightly beyond 1.5phr to about 7.0phr for carbon black and calcium carbonate, and to 3.0phr for zinc stearate. The results suggest that the three fillers can be used at weight fractions of 1.0phr or less, between 1.5 and 7.0phr for carbon black and calcium carbonate, and between 1.5 and 3.0phr for zinc stearate. It must be noted, however, that these conclusions have not taken sample imperfections into account.

Carbon black enhanced the tensile properties of the samples to a greater extent than calcium carbonate, zinc stearate produced an intermediate behaviour. This is in agreement with the conventional classification of carbon black as a reinforcing filler, calcium carbonate as a bulking filler and zinc stearate as a lubricating filler.

Of the three fillers, zinc stearate produces some unique exceptions. At weight fractions below 1.0phr the filler appear to act as a reinforcing filler like carbon black, but between 1.0 and 3.0phr, zinc stearate acts as a bulking filler, similar to calcium carbonate. Beyond 3.0phr, the filler ceases to be reinforcing or bulking. This would suggest that below 3.0phr, fusion and crystallinity are enhanced in the presence of zinc stearate in PVC matrix. But above 3.0phr, the lubricating property appears to predominate.

causing overlubrication.

Normally, reinforcing fillers achieve their effect through adequate interaction of the filler with the polymer molecules. Bulking fillers on the other hand interact only minimally with polymer molecules, however, the interaction improves with increase in shear intensity as observed with calcium carbonate-filled high-shear (HUC) samples. Plasticisation, also appears to have improved the interaction of the filler with the resin, this would explain the enhancement of tensile properties observed with plasticised calcium carbonate-filled (LPC) samples. This effect was more prominent with plasticised calcium carbonate-filled samples than carbon black-filled samples.

5.3.3 Influence of Plasticisation

Plasticisation naturally lowered the values of fracture stress and also increased the values of elongation at break by its softening action on the polymer. However, it appears that plasticisation performed the dual role of softening and toughening the samples.

Plasticisation reduced the differences between the initial fracture toughness of both the low- and high-shear samples by promoting orientation within the low-shear samples. The enhanced orientation may be responsible for the observed toughening action.

5.4 Recommendations for Further Study

In order to elucidate the mechanism of action of zinc stearate in PVC systems, it is recommended that a detailed study be carried out at weight fractions between 0 and 5.0phr, so that the polymer-filler characteristics will be fully understood.

Also, to properly understand and appreciate the influence of mixing shear regime in PVC systems, the study on the high-shear samples should be repeated but this time, the formulations should be compounded under the suggested processing conditions so that the quality of the samples will be improved. Future works should incorporate microscopy, particularly electron microscopy to enable visual examination of the polymer-filler bulk phase structure and possibly sheared domains.

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APPENDIX I

Variations in Equilibrium Sorption Values of the Unplasticised Samples with Increasing Filler Concentration.

Filler Concentration	Equilibrium Sorption (%)				
	LUC	LUB	LUZ	HUC	HUB
0	143	143	143	181	181
0.05	168	139	172	167	167
0.10	152	160	181	147	176
0.30	170	153	173	172	149
0.50	180	163	160	161	173
1.00	163	152	157	155	158
1.50	160	148	166	151	143
3.00	162	153	162	163	150
5.00	168	155	149	163	151
10.00	147	143	136	146	138

APPENDIX II

Variations in Equilibrium Sorption Values of the Plasticised Samples with Increasing Filler Concentration.

Filler Concentration	Equilibrium Sorption (%)		
	LPC	LPB	HPB
0	103	103	-
0.05	121	123	124
0.10	106	104	109
0.30	122	101	114
0.50	130	99	111
1.00	116	103	103
1.50	111	99	103
3.00	116	103	112
5.00	117	106	110
10.00	105	93	103

APPENDIX III

Variations in Specific Gravity Values of the Unplasticised Samples with Increasing Filler Concentration

Filler Concentration	Specific Gravity				
	LUC	LUB	LUZ	HUC	HUB
0	1.30	1.30	1.30	1.38	1.38
0.05	1.36	1.44	1.33	1.34	1.29
0.10	1.35	1.40	1.37	1.35	1.28
0.30	1.35	1.34	1.41	1.27	1.17
0.50	1.34	1.43	1.45	1.37	1.26
1.00	1.34	1.30	1.58	1.27	1.17
1.50	1.34	1.32	1.45	1.30	1.22
3.00	1.35	1.31	1.34	1.34	1.29
5.00	1.35	1.32	1.30	1.35	1.30
10.00	1.35	1.32	1.26	1.36	1.31

APPENDIX IV

Variations in Specific Gravity Values of the Plasticised Samples with Increasing Filler Concentration.

Filler Concentration	Specific Gravity		
	LPC	LPB	HPB
	1.27	1.27	-
0.05	1.23	1.26	1.27
0.10	1.23	1.25	1.21
0.30	1.28	1.21	1.22
0.50	1.22	1.21	1.27
1.00	1.22	1.21	1.19
1.50	1.23	1.22	1.19
3.00	1.24	1.22	1.20
5.00	1.24	1.22	1.22
10.00	1.24	1.22	1.23

APPENDIX V

Variations in Fracture Stress Values of the Unplasticised Samples with Increasing Filler Concentration

Filler Concentration	Fracture Stress (mPa)				
	LUC	LUB	LUZ	HUC	HUB
0	6.3	6.3	6.3	9.5	9.5
0.05	6.2	6.7	8.7	11.3	15.1
0.10	6.4	8.0	8.7	12.9	16.2
0.30	6.5	8.0	8.9	17.5	19.0
0.50	7.0	9.7	9.2	18.6	21.8
1.0	7.2	7.7	8.6	12.1	6.6
1.5	6.6	8.5	6.8	13.2	7.5
3.0	7.1	9.2	4.8	14.0	8.3
5.0	7.2	8.8	4.2	13.9	8.2
10.0	7.2	6.8	3.4	11.5	6.4

APPENDIX VI

Variations in Fracture Stress Values of the Plasticised Samples with Increasing Filler Concentration.

Filler Concentration	Fracture Stress (mPa)		
	LPC	LPB	HPB
0	2.4	2.4	-
0.05	3.0	3.3	1.9
0.10	3.1	2.8	2.7
0.30	3.3	2.4	2.7
0.50	2.5	2.8	3.4
1.00	2.4	2.7	2.7
1.50	2.4	2.7	2.8
3.00	2.7	2.8	2.1
5.00	2.4	2.5	2.6
10.00	2.1	2.5	2.4

APPENDIX VII

Variations in Elongation at Break Values of the Unplasticised Samples with Increasing Filler Concentration.

Filler Concentration	Elongation at break (%)				
	LUC	LUB	LUZ	HUC	HUB
0	1.8	1.8	1.8	2.8	2.8
0.05	1.9	1.8	1.5	3.0	1.8
0.10	1.4	1.9	1.8	3.9	2.0
0.30	1.6	2.1	2.3	1.9	1.7
0.50	1.5	2.7	2.4	1.6	1.6
1.00	1.7	1.8	1.5	1.3	1.5
1.50	1.8	2.2	1.7	1.1	1.6
3.00	1.8	2.3	1.4	1.5	2.4
5.00	1.7	2.1	1.2	1.4	2.3
10.00	1.8	2.0	0.8	1.2	2.0

APPENDIX VIII

Variations in Elongation at Break Values of the Plasticised Samples with Increasing Filler Concentration.

Filler Concentration	Elongation at Break (%)		
	LPC	LPB	HPB
0	573	573	-
0.05	411	411	218
0.10	360	392	253
0.30	456	393	362
0.50	602	433	373
1.00	478	347	316
1.50	404	404	404
3.00	352	222	236
5.00	402	247	247
10.00	352	209	164

APPENDIX IX

Variations in Yield Stress Values of the Plasticised Samples
with Increasing Filler Concentration.

Filler Concentration	Yield Stress		
	LPC	LPB	HPB
0	0.8	0.8	-
0.05	1.7	1.9	1.2
0.10	2.1	1.6	1.9
0.30	1.7	1.1	1.7
0.50	0.9	1.6	2.0
1.00	0.9	1.4	1.6
1.50	1.1	1.4	1.5
3.00	1.3	1.7	1.5
5.00	1.2	1.6	1.6
10.00	1.2	1.6	1.9