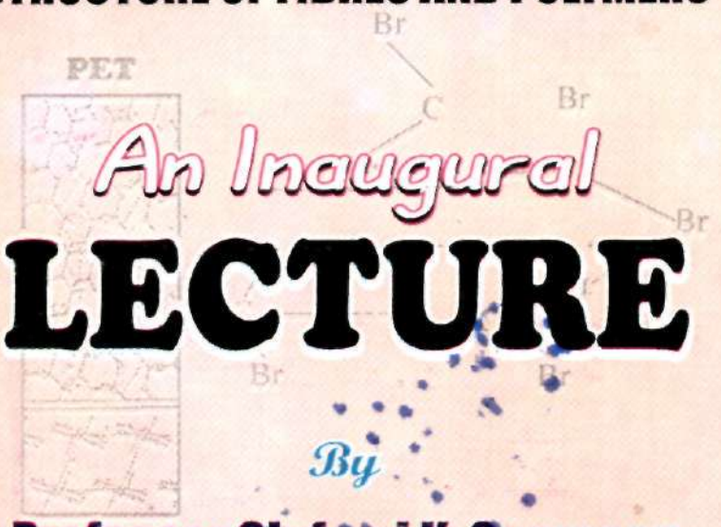
ADDITIVES AND THE SUPRAMOLECULAR STRUCTURE OF FIBRES AND POLYMERS



An Inaugural

LECTURE

By

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23rd January, 2008

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DEPARTMENT OF TEXTILE SCIENCE

AND TECHNOLOGY

AHMADU BELLO UNIVERSITY

ZARIA - NIGERIA

WEDNESDAY 23rd JANUARY, 2008

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ACKNOWLEDGEMENTS

First and foremost, I give thanks to the Almighty God for his grace upon my life and for seeing me through from an inauspicious beginning to this point in my life. Lord, I thank you.

I wish to express my profound gratitude to those I consider my "fathers" in the subject areas of fibres and polymers. In this regard, Emeritus Professor J. Eric McIntyre of the School of Textile Industries, Leeds University deserves special mention. He is a mentor, father and friend. Drs. Ian Holme and George East who were co-supervisors of my research project at Leeds contributed immensely to my professional development and I am very grateful to them both. Late Professor Charles Hugh Giles of blessed memory and George T. McAleese of Strathclyde University Glasgow kindled my interest in fibre-additive interactions generally. They both deserve special thanks. I would like to thank all my colleagues in the Department of Textile Science and Technology, A.B.U. Zaria, for the joy of working together.

I must appreciate my wife Mrs. Ifelayo Sunmonu and the first branch of my "extended" family – Tokunboh, Agnes and Ayodele, for the love and joy they have given me over the years.

My other children, Olufunmilayo, Olakunle and Olukemi have encouraged me to "bend down" when the "going was rough." Thank you for your encouragement and for giving me the joys of fatherhood. I wish to also express my gratitude to all my friends, relations and loved ones for being so supportive in all my life's endeavours. God bless you all.

Last but not the least, I wish to express my sincere gratitude to the Vice-Chancellor, Prof. S.U. Abdullahi, the Chairman of the

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University Organized Lectures Committee, Prof. S.S. Adefila, and other members of the Committee for giving me the opportunity to give this lecture and their assistance in preparing the lecture.

ADDITIVES AND THE SUPRAMOLE CULAR STRUCTURE OF FIBRES AND POLYMERS

PROTOCOLS
The Vice – Chancellor Sir,
Deputy Vice – Chancellors (Academic and Administration)
The Registrar, Dean, Faculty of Science,
Deans of other Faculties
Dean of Postgraduate School, Dean of Student Affairs
Eminent Professors here present, Postgraduate and Undergraduate students here present, Distinguished Guests, Ladies and Gentlemen.

I consider it a great honour and privilege to be given this opportunity to give my inaugural lecture today. This lecture is number nine in the third series of inaugural lectures which is the 26th inaugural lecture of this great university

When I joined the Textile Technology programme of the Kaduna Polytechnic in January 1970, our contemporaries in the Engineering classes taunted my classmates and I with the word 'Auduga' which is the Hausa word for cotton fibre. Having spent the last 38years learning about, researching in, and teaching fibres and textiles, I have come to the realization that there is much more to textiles than Auduga. I hope I can convince you as my lecture unfolds.

SUMMARY

In this lecture, I shall give brief explanations of the key words: Additives, Supramolecular structure, Fibres and Polymers.

In my brief explanations, I shall bring out the usefulness of additives to fibres and polymers generally and especially as these additives increase the utility value of these important engineering and all-purpose materials.

I shall also bring out the importance of Additives, Supramolecular structure, Fibres and Polymers to society in general.
The body of the lecture will concentrate on additives as modifiers of the supramolecular structure of fibres and polymers.

Due to the fact that fibres and polymers are very important engineering and general-purpose materials in the 21st century, my lecture will highlight the importance of these materials especially their current areas of utilization and possible future areas of use. This aspect will be related to their diversity of structure and properties.

Previous research studies in the areas of fibre and polymer/additive interactions will be reviewed briefly to put the lecture in proper perspective.

I shall mention my first contact with the subject areas of additives, fibres and polymers. As a researcher, I shall summarize my research studies (at the doctoral and post-doctoral levels) and modest

contributions to the following important topics as they relate to this lecture:

(i) Fibres
(ii) Polymers
(iii) Fibre and Polymer Additives
(iv) The effect of selected model additives on the supramolecular structure of a selected fibre/polymer.

Finally, I shall reproduce two of my publications that typify the modifying effect of additives on the supramolecular structure of an important polymer/fibre - poly (ethylene terephthalate).

INTRODUCTION

Before explaining the basic terms in this lecture, I want to briefly explain what I understand by Inaugural lecture.
What is an inaugural lecture?
Why give the lecture at all?

My understanding is that Professors are expected to occupy specific chairs of academic disciplines in their respective universities. An inaugural lecture is therefore expected to be given to inaugurate or formally install a Professor in his chair. This is an occasion when a Professor tells the world what he is "professing" in a manner of speaking. The inaugural lecture is expected to be given in the course of a Professor's career in the University. This means that the lecture can be given a year or several years after promotion to the rank of Professor. Inaugural lectures have been used to serve several purposes in Universities world-wide and here in Nigeria. Five major objectives have been identified by (Olaniran, 2002) of the University of Ilorin as follows:

Some inaugural lectures had the objective of addressing contemporary issues which were germane to the progress of society.

Other lectures concentrated on the research activities of the lecturers and their contributions to their discipline. Some other lectures were used as means of addressing academia on important issues of mutual concern. While some other lecturers used their lectures to highlight the contributions of a subject area to modern society. Inaugural lectures have also been used to present progress of activities in a discipline and how these represent contributions to knowledge and society in general.

In the present lecture, I am attempting a very careful blend of some of these noble objectives.

The key words from the title of my lecture are Additives, Supramolecular Structure, Fibres and Polymers

ADDITIVES

An additive is a substance added to another substance or system to achieve a specific purpose (usually a beneficial purpose)

Additives for fibres and polymers are many and varied depending on the fibre/polymer type and the desired purpose the additive is expected to serve.

From a purely utilitarian perspective, important classes of additives for fibres and polymers with direct bearing on this inaugural lecture include:

i. Colorants (Dyes and Pigments)

Dyes are intensely coloured molecules applied to suitable textures of fibrous and polymeric substrates, generally to enhance visual and aesthetic appeal of these materials. Dyes are usually applied in aqueous media. Pigments on the other hand are coloured molecules applied as dispersions in appropriate media. The application of dyes and pigments to fibres and polymers by the industrial processes of dyeing and printing are very important to modern society.

ii. Antioxidants

Antioxidants are additives which are added to fibres and polymers to prevent or inhibit degradative oxidation of these materials as a result of exposure to oxygen. Common antioxidants include phenols, aromatic amines and condensation products of aminophenols with aldehydes, ketones and thio compounds (Billmeyer, 1975).

iii. Flame retardants

These are organic or inorganic chemical compounds added to fibres and polymers to reduce their flammability. These compounds include halogenated phosphates and antimony compounds.

Due to the colossal destruction of life and property from fires emanating from fibres and polymers, flame retardants are very important to research scientists and society at large.

Flame retardant compounds in addition to reducing the flammability of fibres and polymers can also affect the supramolecular structure of these materials, as will be shown later in this lecture

iv. Plasticizers

Plasticizers are important additives usually compounded with polymers with the sole objective of improving the flow and processability of polymers. Plasticizers will also reduce the brittleness of the final product of polymer processing. These result from a phenomenon called plasticization. Plasticization is a direct result of changes in supramolecular structure of fibres and polymers as considered further in this lecture.

v. Sizes (starches)

A size is an additive which is applied as a protective surface coating to yarns to give temporary strengthening of the yarns during weaving operations. Starches extracted from cereals (rice, corn, guinea corn etc.) and tubers such as cassava, yams; etc., and synthetic polymeric sizes constitute another important class of additives for fibres and polymers. Other important additives for major polymers include:

vi. Vulcanizing agents such as sulphur and mercaptans

vii. Accelerators and activators

These classes of additives are used to cross-link rubber molecules to achieve drastic property changes in rubbers

viii, Reinforcing Agents such as particulate and non-particulate (fibrous fillers are used for enhancing mechanical properties of elastomeric, thermoplastic and thermosetting polymers.

ix. Resins

Resins are added to natural fibres to improve their handle and dimensional stability. This list of additives is certainly not exhaustive but it covers the important additives for fibres and polymers especially from the perspective of textile and plastic finishing.

MOLECULAR STRUCTURE

Before considering the term supramolecular structure, I want to briefly mention the importance of chemical structure. Chemical structure is of fundamental importance in any consideration of chemical substances. Without stable chemical structures, all matter in the universe cannot hold together. So how can chemical structure be visualized in relation to supramolecular structure? Chemical structure can be visualized starting from the atomic level. Atoms of elements such as carbon and hydrogen will combine by covalent bonding in a simplified model in Figure 1.

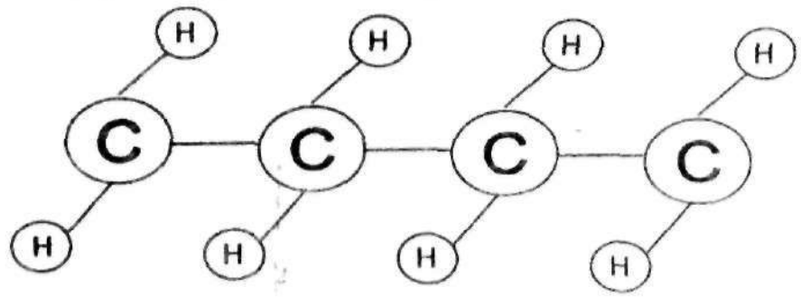
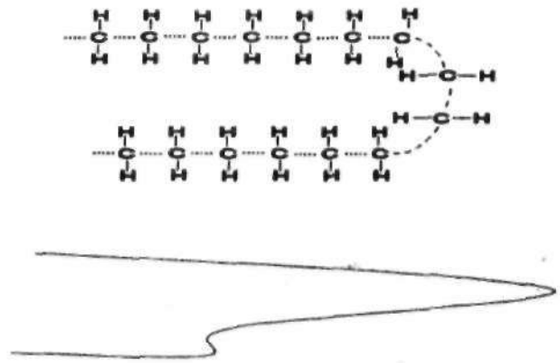


Figure 1:- Atoms of Carbon and Hydrogen in a simple model

This is structure at the atomic level which we can describe as sub-microscopic structure.

This can be visualized for both monomolecular and macromolecular substances. By monomolecular, we mean substances that contain simple molecules in discrete structures such as acids, alkalis and alcohols.

Macromolecular substances on the other hand contain simple molecules forming a chain in a large molecule. (Figure 2a). For macromolecular substances such as polymers, Figure 2a can be visualized as a linear chain.(Figure 2b).



Figures 2 (a) and (b) Single chain of polymer molecule

Several polymer chains will come together to form supramolecular structures. (Figure3). These structures are amenable to modifications by additives.



Fig. 3: Supramolecular structure in Fibres (Hearle, 1963)

So what is supramolecular structure?

SUPRAMOLECULAR STRUCTURE

Supramolecular structure refers to molecular structures formed and stabilized not by covalent bonds but by either specific or non-specific interactions such as hydrogen bonding, hydrophobic forces, van der Waals forces etc.

Supramolecular structures are therefore agglomerates of polymer single chains stabilized by a variety of these aforementioned intermolecular interactions. Structures stabilized by bond strengths

(energies) below 10kJ/mole are generally considered molecular interactions and not chemical reactions. We can therefore use the terms supramolecular structure and molecular interactions interchangeably.

"FINE" STRUCTURE

These supramolecular structures have also been described as 'fine' structure in fibre and polymer technology (Hearle, 1963) Fine structure can also be used interchangeably with supramolecular structure. Because of the possibility of misunderstanding the term 'fine' , I shall restrict myself to the use of supramolecular structure in this lecture.

The subject matter of supramolecular structure has gained some level of importance in the last two decades, so much so that there is now a relatively new area of chemistry known as Supramolecular Chemistry.(Wikipedia, 2007)

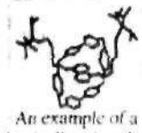
SUPRAMOLECULAR CHEMISTRY

Supramolecular Chemistry is the area of chemistry that focuses on the noncovalent bonding interactions of molecules. (Lehn,1993, 1995), while traditional chemistry focuses on the covalently bonded molecules. Supramolecular chemistry examines the weaker and reversible noncovalent interactions between molecules. As mentioned earlier on, these forces include hydrogen bonding, metal coordination, hydrophobic forces, van der Waals forces, pi-pi interactions and electrostatic effects. Important concepts that have been demonstrated by supramolecular chemistry include molecular self-assembly, folding, molecular recognition, host-guest chemistry,

mechanically- interlocked molecular architectures, and dynamic covalent chemistry. (Gennady et al, 2007) The study of noncovalent interactions is crucial to the understanding of many biological processes from cell structure to vision that rely on these forces for structure and function. Biological systems are often the inspiration for supramolecular research.



An example of supramolecular assembly reported by Jean – Marie Lehn and coworkers in Angew. Chem., Int. Ed. Engel. 1996,35, 1838 – 1840.



An example of a mechanically – interlocked molecular architecture in this case a rotaxane reported by Stoddart and cowokers in the Eur.J. Org. Chemi 1998, 2565-2571



An example of a host – guest chemistry reported by Sanders and cowokers in Angew. Chem., Int. Ed. Engl. 1995, 34, 1096

FIBRES

Fibres are long and thin substances whose ratio of minimum diameter to maximum diameter is very low compared with the ratio of the length to minimum diameter (Sunmonu, 2001)

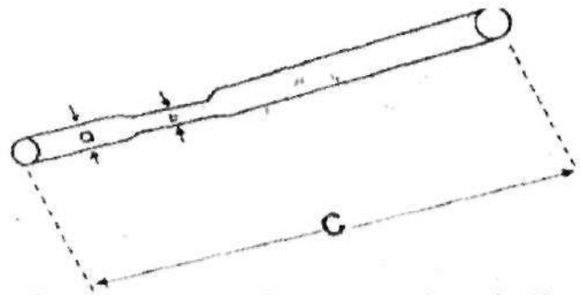


Fig. 4: Diagrammatic Representation of a Fibre

Most common textile fibres consist mainly of polymeric molecules which macromolecular chains are oriented in the direction of the fibre's main axis. Exceptions to this are glass fbres, asbestos fibres, metal fibres and optical fibres.

Natural fibres include cotton, (Auduga) wool and silk. Synthetic fibres include polyamides, polyesters and polyacrylics

POLYMÊRS

Polymers have been defined simply as large molecules that contain recurring structural units (monomers or monomer residues), repeated many times within each large molecule. Natural polymers which always occur as fibres include cellulose, wool keratin and silk fibroin Synthetic polymers which can be fabricated into fibres or plastics include polyethene, polyamides, polyacrylics and polyesters. In this inaugural lecture, I am looking at additives for fibres and polymers.

Several questions then arise.
Why apply additives to fibre/polymer systems?
What do additives do to fibres and polymers?
Why study the modifying effects of additives on fibres and polymers?

Additives are applied to fibres and polymers to achieve purely practical utilitarian purposes as outlined above. Such purposes include improved coloration, flame retardance and other fibre,

textile and plastic "finishing" treatments. In addition to achieving these aforementioned purposes, these additives also serve as important molecular modifiers .

But what do we stand to gain by studying the effect of additives on the supramolecular structure of fibres and polymers?

Why study additives in relation to fibres and polymers? We can answer these questions from two different, but important perspectives.

i. Practical utilization perspective: Here we are interested in what an additive will do to fibres and polymers to increase their utility value.

ii. Supramolecular structure and properties modification perspective.

In this case, we want to know how additives will modify the structure and properties of fibres and polymers. We must also note here that when we modify the structure and properties of our fibres and polymers we can also increase their areas of utilization.

i. Practical utilitarian perspective

Colorants (Dyes and Pigments) will improve the colour and aesthetic appeal of fibres and polymers generally.

Antioxidants will prevent or inhibit oxidation of fibres and polymers. Flame retardants will reduce the flammability of fibres and polymers. Plasticizers will improve the flow and processability of fibres and polymers.

Some polymers such as natural rubber (an elastomeric polymer) is almost completely useless without the addition of vulcanizing agents and other rubber processing additives.

Additives are therefore of paramount importance in fibre and polymer processing and utilization.

ii. Supramolecular structure and properties modification perspective

In this lecture, I am looking at additives for fibres and polymers first, as modifiers of:

- Supramolecular structure
- Macromolecular properties

Secondly as:

- Special aids to improve industrial fabrication techniques
- As materials added to extend areas of utilization of fibres and polymers.

Employing this second perspective therefore, I attempt in this inaugural lecture a concise summation of my involvement in research and publications at the undergraduate, postgraduate and post-doctoral levels, highlighting my modest contributions to knowledge in these all important subject areas of fibres and polymers.

My first academic study of additives to fibres and polymers was carried out between 1975 and 1977 during my undergraduate course at the Strathclyde University, Glasgow, Scotland. (Sunmonu.1975) Here I examined at a very rudimentary level the effects of what are

described as "carriers" on the dyeing and fastness properities of disperse dyes on the polyester component of a polyester/cotton blend fabric.
The result of my study showed that, as expected, the rate of dyeing increased with increase in concentration of carrier as a result of modifications of the supramolecular structure of the polyester fibre. "Carriers" are known to swell and open up polymer structure. This initial foray kindled my interest in the area of the effect of additives on the supramolecular structure of fibres and polymers. This led to my research titled**"The interaction of model flame retardants with polyester fibre"** for my Ph.D at the University of Leeds, England between 1977 and 1982.

For my doctoral research, the interactions of a selection of model flame retardants with poly (ethylene terephthalate) (PET) fibres were studied (*Sunmonu*,1982). The first part of that study comprised a general introduction, methodology, a literature survey of the interactions of simple compounds with PET fibre, and the desorption of compounds from PET fibre. The second part described the experimental techniques, results and discussion. The last part was devoted to a general discussion of the results and conclusion.

The experimental portion of the work was sub-divided into two interconnected sections:

***Section* I.**
The interactions of model flame retardants with polyester fibre

Section **II.**

The interactions of model compounds.
On the basis of this experimental work, it was possible to suggest the type of interactions between the model flame retardants and polyester fibre.

The model flame retardants studied include:

i. Triphenyl phosphate (TPPA)
ii. Triphenyl phosphite (TPPI)
iii. Trixylyl phosphate (TXP)
iv. 1,2,5,6,9,10 – Hexabromo cyclo dodecane (Pyrovatex 3887) (HBD)
v. Tris (2,3 dibromo propyl) phosphate (TBPP)
vi. Tris (2,3- dicholoro propyl) phospate (TCPP)

From the desorption studies, 1,2,5,6,9,10 – hexabromo cyclo dodecane (Pyrovatex, 3887 HBD) appeared to be retained by the fibre to a greater extent than all the other compounds studied. High initial add-on of the flame retardants tended to lead to an increase in both the rate of desorption and the total amount desorbed. The results of Limiting Oxygen Index (L0I) studies have demonstrated conclusively that Tris (2,3- dibromo propyl) phosphate (TBPP) was the most effective flame retardant of those studied for polyester fibre on weight basis.

The thermal analysis data of the PET plus flame retardants suggested that four of the model flame retardants studied (namely TPPA, TXP, TBPP, and TCPP) had the same effects (on a volume basis), on the depression of Tg of PET. Pyrovatex 3887 (HBD) showed a different effect on the depression of Tg. A leveling – off

was observed in its depression of Tg as a function of volume fractions plot.

The effects of the compounds on the depression of Tc and Tm did not appear to follow any particular trend or depend on any aspect of additive molecule.

In order to ascertain the particular functional groups responsible for the interactions between polyester and the model flame retardants, a study was made of the interactions of selected model halogeno – alkyl compounds representative of functional groups in some flame retardants for PET with a model ester (dibutyl terephthalate) representing the PET. From the three methods employed in the study of interactions of model compounds, it was obvious that specific intermolecular interactions were absent in between the model esters and model halogeno-alkly compounds. This however did not preclude the manifestation of weaker, non – specific interactions operating between the model esters and model halogeno alkyl compounds

The formation of supramolecular structures could therefore not be ruled out. This aspect is shown in the two publications at the end of this lecture.

After completing my doctorate degree in 1982, my post-doctoral research activities from January 1982 to date have concentrated mainly on additives as the main modifiers of supramolecular structure, surface properties, fabrication techniques and areas of utilization of fibres and polymers.

IMPORTANCE, CONVENTIONAL AND NEWER AREAS OF USE OF FIBRES AND POLYMERS

Fibres and polymers are of utmost importance to modern living. Fibres are the basic components of most textile yarns and fabrics. Polymers on the other hand are the starting materials for a myriad of engineering and general – purpose applications. A life without contact with and use of these two classes of materials is a practical impossibility in the world today. Due to their diversity of structure and properties, the most important aspects of life in the modern world depend solely on fibres and polymers.

Therefore, the subject areas of fibres, textiles and polymers are of paramount importance to society today.

Conventional uses of fibres and polymers in the modern world include food, food packaging, clothing, building materials, automotive parts, floor covering, agricultural geo-technical materials etc.

Newer areas of use for fibres and polymers include medical implants, artificial human organs, aerospace and ablative fabrics etc.

Possible future areas of utilization of fibres and polymers will depend on microtechnology and nanotechnology.

Research activities in fibres

Characterization studies are very important in any attempt to obtain natural fibres from local flora and fauna in any country. Research

studies initiated to source natural cellulosic fibres from flora and fauna native to Nigeria include (Sunmonu and Abdullahi, 1990); (Sunmonu,2003,a, b, c & d); (Sunmonu,2005); (Sunmonu,Harrison and Eze,2004) This area of research holds promise for replacement of conventional fibres with newer and better fibres.

Derivation of man-made fibres from suitable intermediates of the petrochemical industries is a another focus of research on fibres and polymers. (Sunmonu, 1989, 1993).

Research activities in polymers

Research studies which relate to functional groups present in polymers, and their interactions help in elucidating beneficial and deleterious reactions. Such studies have shown that functional groups present in dyes, fibres and polymers have a controlling effect on the dyeability of these substrates. (Bello, Peters, Nkeonye and Sunmonu, 2002); (Bello, Peters, Nkeonye, Sunmonu and Abdulrahman, 2005). Accelerated photo oxidation induced by selected chemicals for certain polymers such as polyethene, may be beneficial to the environment. (Sunmonu and Dalhat, 2004).

Research activities in fibre and polymer additives

Starches as extracted can be utilized as sizes and stiffening agents on textile fibres (Sunmonu and Ogunribido, 1995).

Acid – modified starches can give better results even at lower costs as shown by some relatively recent studies. (Sunmonu and Ogunribido, 2007)

Intense research activities (Reeves,1974; Aenishaeslin,1974, Weil,1978) on the mechanisms of flame retardation and selection of reagents to suite specific fibres and polymers have brought about a better understanding of this subject area. A new and important area of fibre/polymer-additive studies is the incorporation of particulate and fibrous fillers into resinous polymers to give composites. Materials with massively improved physical and mechanical propertiess have resulted. (Sunmonu, 2002; Sunmonu, 2006) (Adamu and Sunmonu, 2008), (Adamu 2008)

Consequently, composites have now become one of the new frontiers of research in fibres and polymers (Sunmonu,2007).

Research studies of previous workers in the area of polymer-additive interactions which formed the 'template' upon which my own researches were grafted include the following.

The interactions of organic liquids with polymers as indices of changes in supramolecular structure have been studied extensively over the last sixty five years. For example, (Gee and Treloar,1942) investigated the swelling of rubber in benzene. (Richards, 1946) studied the swelling of polyethene in some organic solvents. In these first series of studies, attempts were made to correlate modifications of the supramolecular structures of the polymers in these liquids with thermodynamic parameters such as the Heat of Dilution, Gibbs' Free Energy of Dilution, and the Entropy of Dilution and solution. From these earlier studies, it was possible to express the degree of swelling (Q) as a function of the expression shown below:

$$\sqrt{v_o} \; \phi \; \left(\sqrt{E_o / v_o} \; - \; \sqrt{Er/vr} \right) \quad --(1)$$

Where E_o/V_o = Cohesive Energy Density of the solvent
E_r/V_r = Cohesive Energy Density of the polymer
V_o = Molar volume of the solvent

Swelling was found to be at a maximum in solvents for which the above expression was zero, i.e when E_o/V_o and E_r/V_r are equal. On closer examination of equation (1), it is easy to see the beginnings of the solubility parameter concept as a means of showing the interaction of liquids with polymers, and changes in the supramolecular structure of the polymers.

(Moore, 1947) studied the interactions of nitrocellulose with mixtures of organic solvents such as ethyl alcohol, benzene and hexane. Using microscopic examination, he was able to correlate the equilibrium swelling of the polymer with the concentration of the solvent mixtures. The results of Moore's work showed that with increasing concentration of solvent, the fibres are becoming progressively swollen until at a certain concentration, depending on both constituents of the mixture, solution occurs. For a limited range of solvents, the study was able to relate the swelling of nitrocellulose to the Cohesive Energy Densities of the solvents.

(Mandelkern and Long, 1951) and (Hartley, 1949) studied the kinetics of sorption of organic liquids by cellulose acetate. These studies attempted to correlate the rate of sorption and equilibrium

sorption with the vapour pressure of the liquid, fibre thickness and temperature.

The first major series of investigations of the interactions of organic liquids with poly (ethylene terephthalate) were carried out between 1961 and 1964 by (Sheldon et al, 1961, 1962, 1963, 1964) in Bradford. By measuring the swelling and crystallinity of PET, Moore and Sheldon were able to show that the kinetics of crystallization and the equilibrium crystallinity and swelling were dependent on a number of factors which include the molecular size of the liquid, polarity, type and solubility parameter of the liquid. These factors are good indices of studying supramolecular structural changes in fibres and polymers. Conclusions that have emerged from these studies are:

i. That polymer crystallization is diffusion –controlled
ii. That the solubility parameter of a liquid is a very important determinant of the extent of liquid –polymer interaction.
iii. That there may be the possibility of two solubility parameters representing the aliphatic and aromatic parts of the molecule.
iv. That the rate at which the polymer crystallized, and the extent of the crystallization was dependent on the size of the molecules, the smaller the molecules the greater the extent of crystallization.

The next extensive studies of the interactions of organic liquids with PET were initiated by (Weigmann, 1974). Using the solubility parameter principle, these workers were able to explain the

preferential interaction of certain liquids with polyester fibre. They proposed the 'bimodal' nature of the PET repeat unit. The basic idea in their theory proposed that the polyester repeat units appear to have two solubility parameters representing both the aromatic and aliphatic residues.

Other workers in the area of solvent –polymer interactions include (Hartley, 1978) who studied the effects of a number of organic liquids on the physicochemical properties of semi-crystalline filaments of PET. Hartley showed that the shrinkage in the PET filaments was directly proportional to the volume – fraction of the liquid absorbed, and he was able to correlate the magnitude of the shrinkage with the size of the molecules of the liquid, larger molecules giving rise to smaller volume intake and hence smaller equilibrium shrinkage. Hartley's views of the PET – solvent interactions are at variance with the earlier postulations of Weigmann et al. (Khan, 1978) working in India, investigated the interaction of a number of organic solvents with poly (ethylene terephythalate). His results tend to support the earlier work of (Sheldon et al,1961-1964). More studies of the interactions of solvents with PET were carried out by (Ingamells et al, 1973-1980) Their investigations were confined to the plasticization of PET as demonstrated by the lowering of the Glass Transition Temperature (Tg) and by increased dye uptake. (Ingamells and Yabani,) showed that in the swelling and plasticization of PET, 'carriers' did not cause the swelling of undrawn fibres but did cause the swelling of drawn fibres. (Ingamells and Peters) showed that the effectiveness of a 'carrier' in increasing the rate of dyeing of polyester fibres with disperse dyes was dependent on the ability of the 'carrier' to reduce

the Tg of the fibre and not on its ability to swell the fibre. Furthermore, their results showed that in the diffusion of dyes into polyester fibres, non-polar dispersion forces controlled the plasticization of the fibres.

The studies of Ingamells et al have attempted to explain polymer-additive interactions (supramolecular structure modificatios) in terms of the segmental mobility of polymer chains and the associated 'free volume' of the system. They postulated that carriers increase the 'free volume' and hence the rate of dye uptake.

Emanating directly from my doctoral research studies at Leeds are the following papers 1& 2 reproduced here to illustrate the onset of my modest contributions to the subject area..

1.. Depression of major transition temperatures of poly(ethylene terephthalate) fibre by some model compounds.

2. The desorption of model compounds from polyethylene terephthalate) fibre.

McINTYRE, HOLME AND SUNMONU,1987

Depression of major transition temperatures of poly(ethylene terephthalate) fibre by some model compounds

Abstract

The effect of five flame retardant compounds on the depression of glass-transition temperature (Tg), cold crystllization temperature (Tc), and crystalline melting temperature (Tm) was examined by thermal analysis. The depression of Tg by four of the compounds was linear. The depression of Tg by the fifth compound gave a plateau – type minimum which could be due to 'super –saturation' theory or a modification of Kovacs' theory.[5]

INTRODUCTION

A study of the depression of the glass – rubber transition temperature (Tg) of polymers resulting in their plasticization, constitute a very important aspect of polymer structural studies, especially from polymer processing view point. Several workers[1-10] in this area, have studied different aspects of the problem using specific polymer additive systems. The first major series of investigations of poly (ethylene terephthalate) PET – organic solvent systems, were carried out by Sheldon and co- workers[1-4] who considered the problem from polymer swelling and crystallinity perspectives. Kovacs[5] considered the additivity of the Tgs of polymers and diluents. Ribnick, Weigmannn and Rebenfeld [6-8] examined the effect of organic solvents on the Tg of PET during the processing of PET fibre in organic solvents. Relatively more recent studies by Ingamells and others[9-10] examined PET plasticization, as

manifested by segmental mobility of polymer chains and the "bimodal" nature of PET macromolecular structure in its interaction with specific functional groups in solvents. This paper examines PET plasticization based on a 'super-saturation' theory or a modification of Kovacs' additivity theory.

EXPERIMENTAL

Five model flame retardant compounds Triphenyl phospate, TPP; Trixylyl phospate, TXP; 1,2,5,6,9,10-Hexabromocyclododecane, HBD; Tris-(2,3-dicholopropyl) phospate, TCP; and Tris –(2,3-dibromopropyl) phospate, TBP were applied to poly (ethylene terephthalate), PET fibre by high temperature (140^0C) 'dyeing' from their aqueous emulsions. The transition temperatures (Tg, Tc and Tm) of the treated samples and untreated controls were measured using Differential Scanning Calorimetry (DSC) at a heating rate of 10^0C/min. All readings were taken on quenched samples because the enthalpy peaks of the second and subsequent runs on the DSC were better defined than the first runs.

RESULTS

Thermo analytical data for the fibres treated with the five compounds and the untreated controls are given in tables I-V and figures 1 and 2. The add-ons (%) were first obtained by weight difference of samples before and after high temperature 'dyeing''. The add-ons were then converted to volume and mole fractions.

Table 1 **Triphenyl phosphate (TPP)**

(a)

Volume fractions		Tg Onset
PET	**TPP**	**Temp (^{0}C)**
1.0	0.0	75
0.989	0.014	70
0.979	0.021	68
0.959	0.041	65
0.946	0.54	55
0. 918	0.82	48
0.881	0.119	48
0.829	0.171	30

(b)

Mole fractions		Tc peak	Tm Peak
PET	**TPP**	**Temp (^{0}C)**	**Temp (^{0}C)**
1.0	0.0	131.5	255.5
0.989	0.011	139	255
0.983	0.017	116	255
0.968	0.032	120	244.5
0.958	0.042	119	253
0.936	0.064	107	251
0.905	0.095	105	249
0.863	0.317	82.5	247

Table II Trixylyl phosphate (TXP)

(a)

Volume fractions		Tg Onset
PET	TPP	Temp (^{0}C)
1.0	0.0	75
0.9547	0.0451	63
0.9071	0.0929	55
0.8930	0.107	46
0.8779	0.1221	46
0.8577	0.1423	42

(b)

Mole fractions		Tc Peak	Tm Peak
PET	TXP	Temp (^{0}C)	Temp (^{0}C)
1.0	0.0	131.5	255.5
0.9815	0.0185	114.5	254
0.9610	0.039	113	254
0.9542	0.0458	106	244.5
0.9475	0.0525	107.5	253
0.9378	0.0622	109	251

Table III Tris (2-3-dicholoro propy1) phosphate (TCP)

(a)

Volume fractions		Tg Onset
PET	TPP	Temp (^{0}C)
1.0	0.0	75
0.9741	0.0259	65
0.9552	0.0448	58
0.9216	0.0784	56
0.8859	0.1141	35
0.8496	0.1504	35

(b)

Mole fractions		Tc Peak	Tm Peak
PET	TXP	Temp (^{0}C)	Temp (^{0}C)
1.0	0.0	131.5	255.5
0.9867	0.0133	127	255.5
0.9768	0.0232	123	254
0.9587	0.0413	123	253
0.9388	0.0612	92.5	249.5
0.9178	0.0822	96	250

Table IV Tris (2-3-dibromo propyl) phosphate (TBP)

(a)

Volume fractions		Tm peak
PET	**TPP**	**Temp (^{0}C)**
1.0	0.0	75
0.9986	0.0034	70
0.9937	0.0063	70
0.9926	0.0074	70
0.9908	0.0092	70
0.9812	0.0188	68
0.9615	0.0385	64
0.9347	0.0653	55
0.9256	0.0744	57
0.8993	0.1007	40

(b)

Mole Fractions		Tc Peak	Tm peak
PET	**TBPP**	**Temp (^{0}C)**	**Temp (^{0}C)**
1.0	0.0	131.5	255.5
0.9984	0.0016	126.5	255
0.9971	0.0029	137.5	256
0.9966	0.0034	133.5	256.5
0.9957	0.0043	126	256
0.9912	0.0088	122	254
0.9818	0.0182	118	254
0.9086	0.0314	112	253
0.9641	0.0359	113	253.5
0.9507	0.0493	88	249

Table V: 1,2,5,6,9,10-Hexabromocyclododecane (HBD)

(a)

Volume fractions		Tg Onset
PET	HBD	Temp (^{0}C)
1.0	0.0	75
0.9676	0.0324	67
0.9374	0.0626	65
0.9093	0.0902	65
0.8693	0.1307	65

(b)

Mole Fractions		Tc Peak	Tm peak
PET	HBD	Temp (^{0}C)	(^{0}C)
1.0	0.0	131.5	255.5
0.9906	0.0094	128	255
0.9814	0.0186	123	254
0.9727	0.0273	113.3	253
0.9591	0.0409	118	251.5

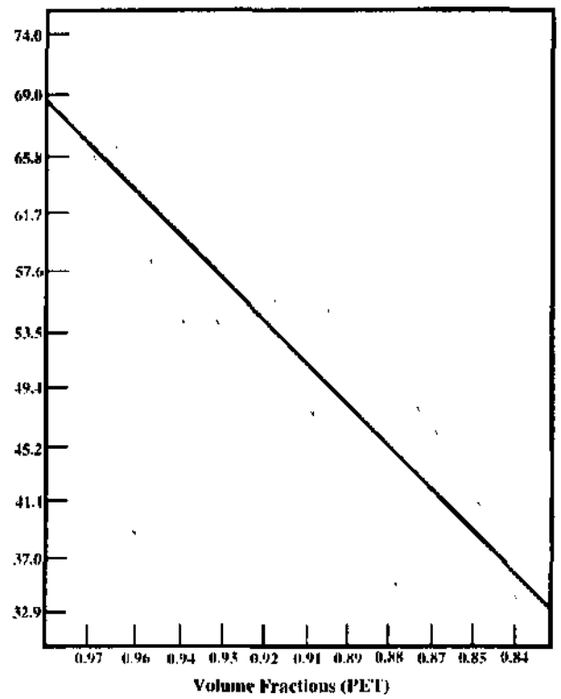


Figure 1 Tg Onset temperatures as a function of volume fractions (PET/HBD)

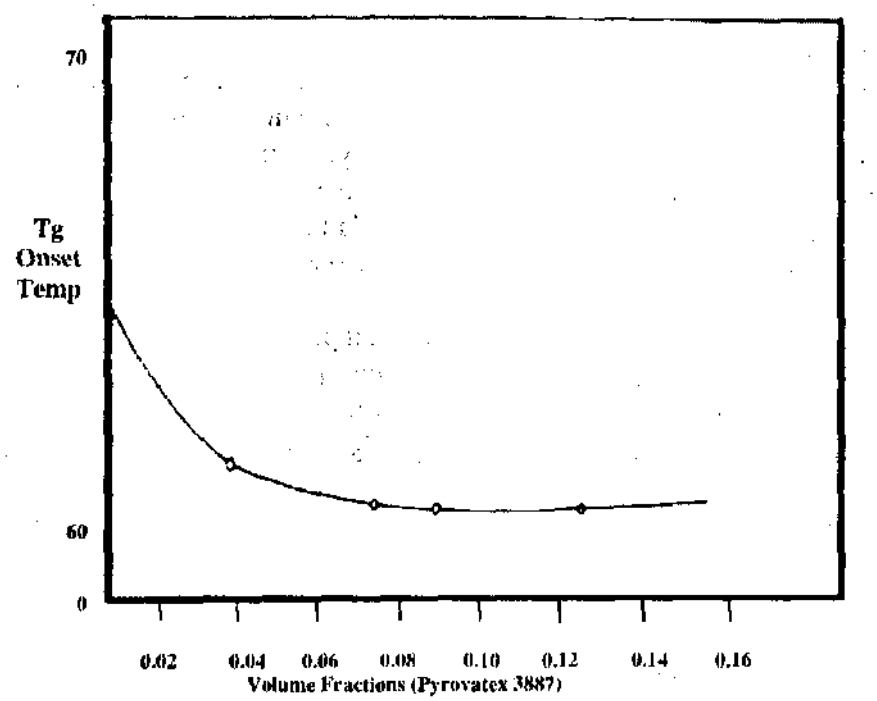


Figure 2 Tg Onset temperatures as a function of volume fractions (PET/IIBI)

The data from Tables I-IV when plotted show that the depression of Tg by the four compounds (TPP, TXP, TCP and TBP) was approximately a straight line as shown in figure1 Tables I-V show that the depression of Tc and Tm by all the compounds will give approximately linear plot with more scatter than Figure 1. The depression of Tg by HBD is different in character, exhibiting a plateau –type minimum beyond quite a low concentration. The results show that an increase in the concentration of the additive in the polymer depresses the Tg of the polymer up to a certain point beyond which further increases in additive concentration does not lead to further depression of the Tg. This behaviour of HBD in the polymer could be due to either of these two explanations.

(I) Based on some fundamental assumptions, Kovacs' theory predicts the Tg in a binary polymer-plasticizer system on the following mathematical relationship

$$x \nabla\alpha_1 (Tg - Tg_1) + (1 - x) \nabla \alpha_2 (Tg - Tg_2) = 0 \qquad (1)$$

Where x = Volume fraction of polymer or plasticizer α_1 and α_2 are constants

Tg, Tg_1 Tg_2, are the Tgs of polymer – plasticizer mixture, plasticizer and polymer respectively.

The relationship in Eq (1) does not depend on free volume since it is invariant at Tg, that is $fg_1 = fg_2 = fgx$.

This means that Tg x is evaluated as a weighted mean of Tg_1 and Tg_2 which are dependent on the constants α_1 and α_2. There is a

critical temperature Tg_c, below which this relationship will no longer hold. Since if
$Tg_2 > Tg_1$ then

$$Tg_c = Tg_2 - \frac{fg_2}{\nabla\alpha_2}$$

Tg_c will depend only on Tg and $\nabla\alpha_1$ of the plasticizer and on fg_2. It therefore means that the lowering of Tg in such a system is not a continuous function of the concentration of the plasticizer. In the PET – HBD system studied, it is possible that the 'Tg' of HBD itself is so low that it is unable to produce any substantial depression of the Tg of PET beyond a certain value. This therefore, means that modifications of the theory of Kovacs[5] could explain this result. It is however, not possible to prove this suggestion since the Tg of HBD could not be measured because the compound could not be quenched to a glass.

(ii) The method of incorporation of the additive is such that the temperature at which it is incorporated is substantially higher than the Tg of the polyester fibre. If the additive is more soluble at the high temperature, it is possible that on leveling, the additive is present in a 'super-saturated' state. In that case the excess of additive over the saturation solubility will no longer be truly dissolved and will cease to have a lowering effect on the measured. Tg.

McINTYRE, HOLME AND SUNMONU,1987

The desorption of model compounds from poly(ethylene terephthalate) fibre

Abstract

The desorption of a selection of model flame retardant compounds from poly (ethylene terephthalate), PET fibre was studied. The compounds were applied to PET fabrics by high temperature 'dyeing' and the fabrics subjected to ten consecutive washing cycles in the Society of Dyers and Colourists (SDC), wash-wheel. The desorption results of one of the compounds 1,2,5,6,9,`10, hexabromo cyclo dodecane (Pyrovatex 3887) showed that the rate of desorption is concentration- dependent and a distinct leveling –off effect is observed. This is thought to be explained by a super-saturation theory. This super-saturation theory could lead to Pyrovatex 3887 being present in the PET fibre in a multi-layer form as a result of hydrogen bonding due to self- association.

INTRODUCTION

The rate of, and the equilibrium desorption of additives from fibrous polymers provide an important insight into the durability and usefulness of these additives under normal end-use conditions. Most chemical compounds employed as additives in the textile industry, be they dyes, antioxidants or flame retardants, derive their importance from the fact that they are able to alter (and generally improve) the desirable properties of the different textile fibres. For a compound to be effective as an anti-oxidant or a flame retardant, sufficient quantities of the additive must remain in the fibre after several washing or dry-cleaning cycles. This therefore emphasizes the importance of desorption studies in fibre-additive systems. Of all

textile additives, the desorption of dyes from textile substrates have been studied most extensively. One of the earliest attempts was that of Vickerstaff and Waters who in 1942 investigated the adsorption and desorption of disperse dyes from cellulose acetate fibre. Their results suggested the complete reversibility of the disperse dyeing process. Similar results were obtained by Bird and Manchester[2] in their study of the adsorption isortherms of disperse dyes on cellulose acetate. Other workers [3-8] have studied other aspects of the desorptoin of different classes of dyes from textile fibres.

Calvert and Bilingham[9] in their study of the loss of antioxidants from polyethylene and polypropylene developed mathematical models for desorption from bulk polymer, films an fibres.

The desorption of flame retardants from PET fibres does not appear to have received much attention. Smith[10] studied the effect of multiple laundering cycles on the flammability of polyester fabrics treated with 'firemaster 200' (Michigan Chemical Corporation). His studies showed that the bromine content of the treated fabric decreases during the first ten laundering cycles, but little bromine was lost during the next 40 additional washing cycles. Smith's results further showed that the effects of 50 dry –cleaning cycles were very similar to those of 50 laundering cycles.

Fisher et al.[11] studied the wash –fastness of a number of phosphorus – containing flame retardants on 'crimplene polyester (ICI) and 'melded' polyester fabrics. Their results show that compounds such as Tris- (2,3 dibromopropyl) phosphate and Pyrovatex 3887 have relatively good wash –fastness properties on polyester firbre. This

paper considers the desorption of some model brominated alkyl and organo – phosphorus flame retardant compounds from PET fibre and suggests possible mode of retention of these compounds.

Experimental Technique

A 100% polyester taffeta fabric woven from poly (ethylene terephthalate) filament yarns was selected for investigation. The fabric was scoured and heat –set according to ICI Fibres Manual L7/2. Each sample to be treated was stitched around the edges with a 100% polyester thread using Rimoldi overlock sewing machine. The stitching around the edges of the samples was necessary to prevent fraying and subsequent loss of fibres during the washing cycles. The flame retardant compounds studied were:

1. Triphenyl Phosphate (TPPA)
2. Trixylyl Phosphate (TXP)
3. 1,2,5,6,9,10- Hexa bromo cyclo dodecane (Pyrovatex 3887) (HBD)
4. Tris (2,3 dibromo propyl) phophate (TBPP)

These compounds were used as obtained from the suppliers without further purification. They were emulsified and applied to the suitably prepared PET fabrics.

Application was by the high temperature exhaustion ('dyeing') method. The treated fabric samples were subjected to 10 consecutive washing cycles in the SDC wash-wheel.

Washing conditions

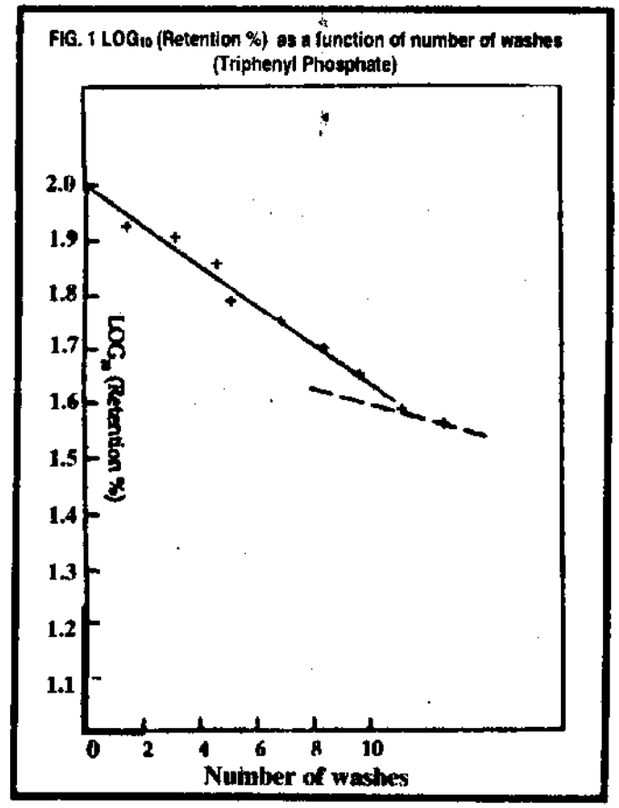
Teepol L (Shell) anionic detergent)	(0.5%)1ml
Water	200 ml
Washing temperature	60^0C
Washing time	30mins

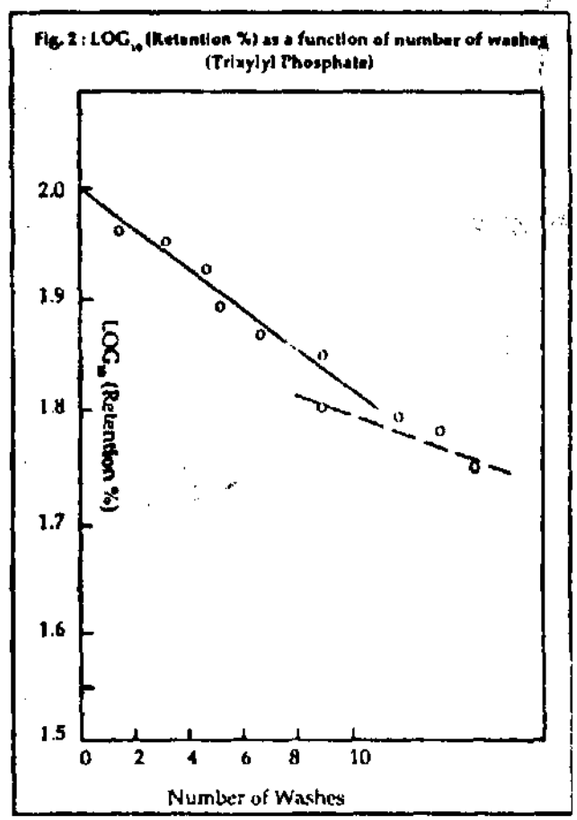
The washed samples were each rinsed separately in cold water and dried in an air oven at 60^0C. The samples were then kept in a standard conditioning atmosphere for 24 hours before weighing.

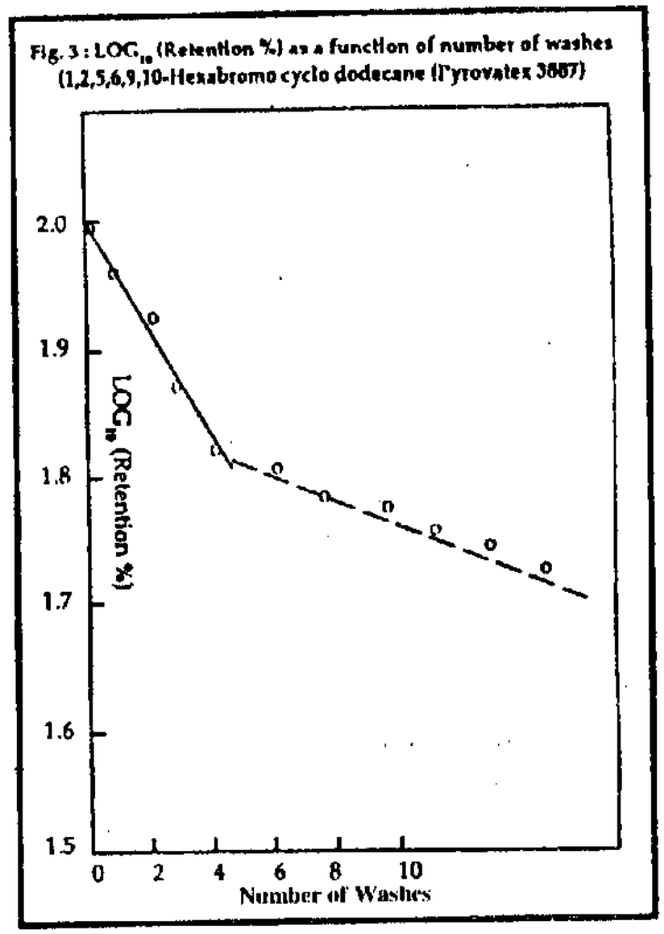
RESULTS

The results are shown in Figures 1 to 6. and Tables 1 and 2.

FIG. 1 LOG_{10} (Retention %) as a function of number of washes (Triphenyl Phosphate)




Fig. 2 : LOG10 (Retention %) as a function of number of washes
(Trixylyl Phosphate)
2.0
1.9
1.8
1.7
1.6
1.5
LOG10 (Retention %)
0
2
4
6
8
10
Number of Washes


Fig. 3 : LOG10 (Retention %) as a function of number of washes
(1,2,5,6,9,10-Hexabromo cyclo dodecane (Pyrovatex 3887)
2.0
1.9
1.8
1.7
1.6
1.5
LOG10 (Retention %)
0
2
4
6
8
10
Number of Washes

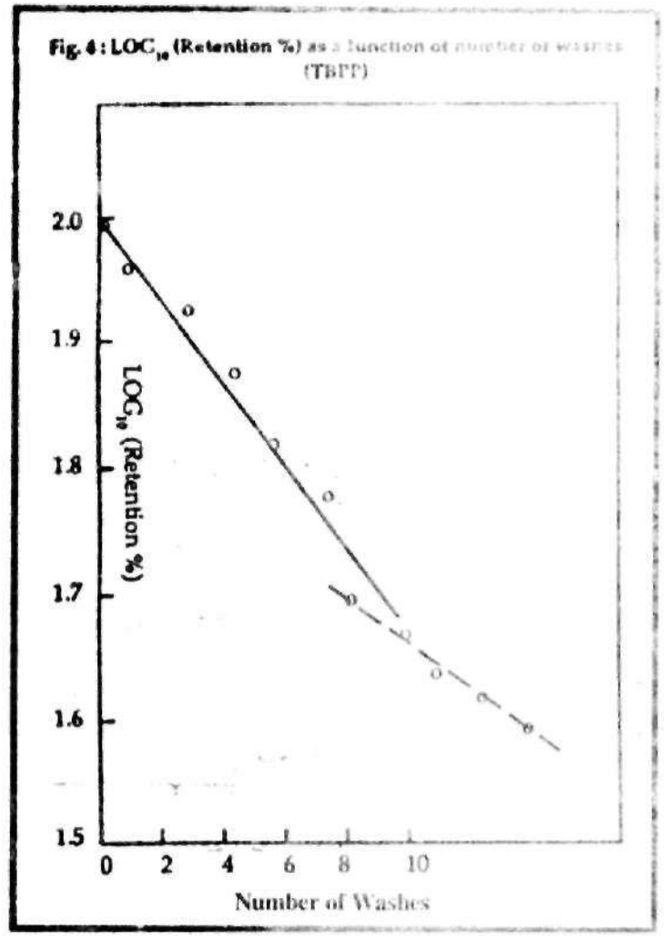

Fig. 4 : LOC10 (Retention %) as a function of number of washes (TBTF)
2.0
1.9
1.8
1.7
1.6
1.5
LOC10 (Retention %)
0
2
4
6
8
10
Number of Washes

Fig. 5: LOC_{50} (Retention %) as a function of number of washes
1,2,5,6,9,10-Hexabromo cyclo dodecane (Pyrovatex 3887)

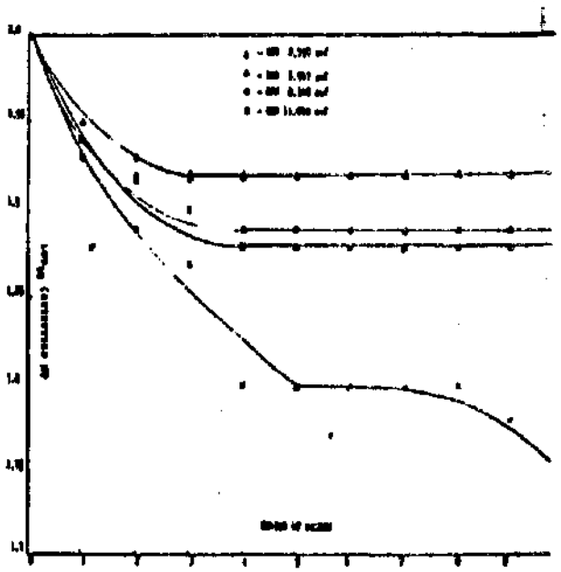


Fig. 6 : Retention % as a function of molecular weight

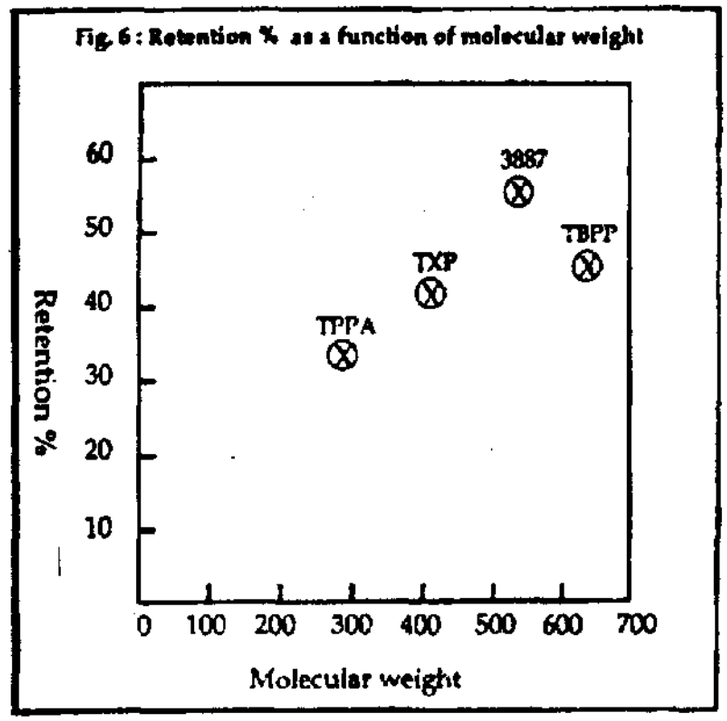


Table 1 Slope of Initial and final portions of Retention Graphs

Figure	Compound	Slope of Initial Portion of Graph	Slope of Final Portion of Graph
1	TPPA	-0.047	-(0.040)*
2	TXP	-0.040	-(0.030)*
3	HBD	-0.044	-(0.017)*
4	TBPP	-0.052	-(0.039)*

*- These values are based on insufficient data to be reliable

Table 2

Retention as a function of molecular weight

Flame Retardant Compound	Molecular Weight	Retention (%)
Triphenyl phosphate (TPPA)	326.29	38.9
Trixylyl phosphate (TXP)	413.0	40.22
(Pyrovatex 3887) (HBD)	641.70	52.1
Tris (2,3-dibromo Propyl) Phospate (TBPP)	697.43	41.98

DISCUSSION

Figures 1-5 show the desorption of all the compounds studied as a function of number of washes. The first observation is that the amount of flame retardant compound desorbed per wash is not constant. It can be seen from these figures that for all the compounds

studied, the first washes remove more additive than subsequent washes. Logarithmic plots (Figures 1 to 4) however approximate to straight lines. The Pyrovatex 3887 results (Figure 3) show a change of slope representing two apparent rates of additives loss from the PET fibre. Change of slopes are however not clearly evident in the desorption graphs of the other flame retardant compounds (Figures 1,2 and 4). The slopes of figures 1 to 4 are shown in table 1 Figure 4 shows that for Pyrovatex 3887, the slope of the final portion of the graph indicates that the initial rate of additive loss is greater than the final rate.

The changes of slope in the $\log_{10}$ retention graph of Pyrovatex 3887 leads to a leveling off of the retention graph, as shown in fig.5. Although the variation in the initial concentration of the flame retardant in the polyester fibre makes direct comparison of the desorption results very difficult, nevertheless some generalizations can be made. Triphenyl phosphate (TPPA) and Tris (2,3-dibromopropyl phosphate (TBPP) have moderate retention properties on polyester fibre. Of the compounds studied, Pryrovatex 3887 has the best retention properties on polyester fibre followed by Trixylyl phosphate and Tris-(2-3-dichloro propyl) phosphate.

The results suggest that although molecular weight affects the retention properties of the additives studied, it does not play a decisive role. Figure 6 shows that the retention values are not directly related to the molecular weight. For the four compounds investigated (TPPA, TXP, HBD, and TBPP), the retention properties improved slightly with increases in molecular weight. The high molecular weight of Pyrovatex 3887 (641.79) may therefore

contribute to the good retention. Figure 5 shows that for the Pyrovatex 3887, the percentage retention values decrease progressively as the initial additive concentration in the fibre increases. This is not the case with the other four compounds studied.

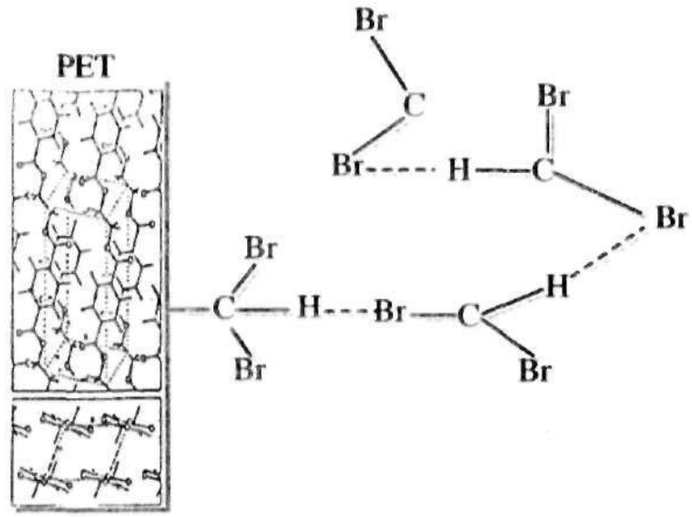
CONCLUSIONS

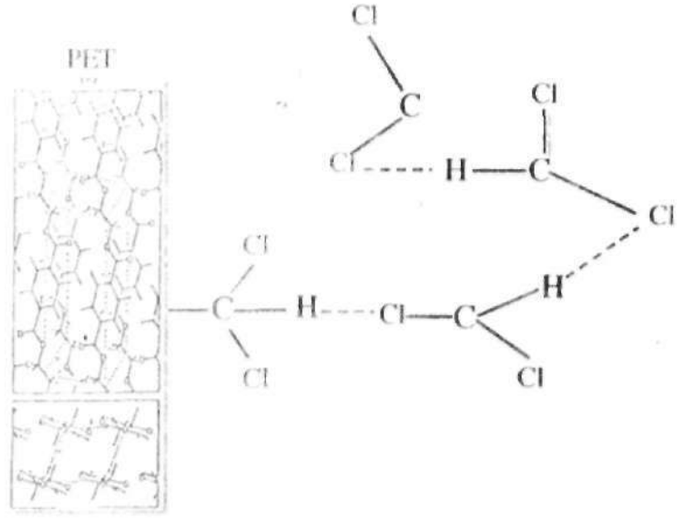
The solubilities of the compounds at different temperatures could explain the concentration dependence of the retention properties of these compounds on polyester fibre. Figure 5 shows that in the PET-HBD system, the sample with 2.5% owf of flame retardant has the best percentage retention. These results could be explained by supposing that high initial additive concentrations mean that the additives are present as super-saturated solutions in the polyester fibre structure. The concept of super-saturation seems reasonable in this instance since the flame retardants were applied at relatively high temperatures. It is therefore possible for the flame retardant compounds to be present as super –saturated solutions in which case they will slowly diffuse to the surface (a process sometimes known as 'blooming').

The results in figure 6 suggest that although the molecular weight of the additives may exert some influence on their retention properties, other parameters of the additive molecule (such as the functional groups present) play more important roles. If the functional groups present in the flame retardants play a decisive role in their retention by polyester fibre, the desorption results can be used as a qualitative index of the interactions between the PET and the different compounds.

Of the groups studied, the brominated alicyclic groups proved to have the best retention properties on PET, and this suggests that there is a relatively strong interaction between these groups and some or all of the polyester structure. Consideration of possible interaction is between C-H groups activated by attachment to bromine, and ester carbonyl groups.

If hydrogen bonding occurs between the alkyl halides, (of the brominated alicyclic groups), as a result of self association as shown below:-





tion. Pyrovatex 3887 could be present in the polyester in **'multi-layer' form, or 'aggregated' form.**

Concluding Remarks

It is obvious that dditives, in addition to modifying properties of fibres and polymers also modify the supramolecular structure of these materials. Studies of such modifications are very useful in developing new additives and this will invariably lead to an increase in the utility value of fibres and polymers. From the foregoing, my research activities at both the doctoral and pos-doctoral levels have given me the opportunity of making my modest contributions to the body of knowledge in the two broad areas of:

- ❖ Fibre/polymer-additive systems
- ❖ Effect of additives on the supramolecular structure of fibres and polymers.

The question may then arise,
What are the benefits accruing from these researches to other researchers in industry and academia?

A better understanding of fibre/polymer-additive systems and the effect of additives on the supramolecular structure of fibres and polyners will bring about the following benefits to other researchers in particular and society at large:

- ♦ Deeper and better understanding of the mode of action of additives on fibres and polymers. That is, the mechanisms of flame retardance, antioxidant action, vulcanizing action, reinforcing action, etc, of additives is now better understood.
- ♦ Deeper and better understanding of the mode of retention of additives by fibres and polymers. That is, the functional groups in fibres, polymers and additives responsible for their anchorage on the substrates is now better understood.

This has now led to the development of newer and better additive formulations for fibres and polymers.(A Richard Horrocks, Min Y. Wang, Mike E Hall, Femi Sunmonu and John S. Pearson, 2000)

Formulations 1: Polymer resin binders

Trade name	Chemical content	Solids content (%)	pH
LA560S	Vinyl chloride/acrylic copolymer	51	0-1
Vinamul 3303	Vinyl acetate ethylene copolymer	52-54	5-6
Vinamul 6975	Vinyl acetate copolymer	54-56	4 -5
Primal E-821	Non-ionic acrylic	60	5-6

Formulation 2: The standard formulation

Component	Wet weight (%)
Polymer resin binder LA560S (Vinyl chloride /acrylic copolymer)	33.0
Plasticizer chlorinated paraffin	9.4
FR additives DBDPO/Sb_4O_3	47.7
Others defoamer thickener etc	9.9

This has also dovetailed to newer areas of research into fibre-reinforced polymer composites. This will invariably lead to the development of new and better engineering materials from conventional fibres and polymers. (Sunmonu and Kogo, 2007).

Finally, our newly initiated fibre-filler interphasal (interphase and interface) studies may lead to the development of useful materials using nanotechnology.

Thank you for your attention.

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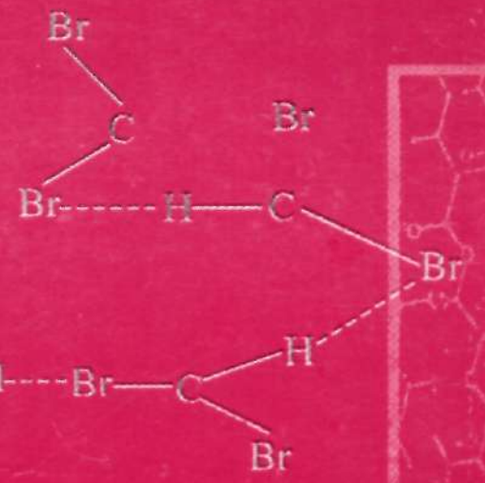
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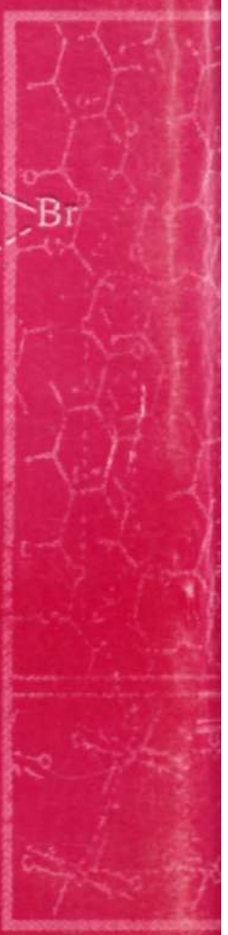
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