Inhibiting the deterioration of plasticized poly(vinyl chloride) – a museum perspective

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Preface and acknowledgements

The Ph.D. study presented was organised as a collaboration between The National Museum of Denmark and the Technical University of Denmark (DTU). It constitutes the research requirement for the Danish Ph.D program in Chemical Engineering. Most of the research was carried out in the laboratory in the Department of Conservation in Brede.

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Yvonne R. Shashoua
Copenhagen, September 2001

1. Abstract

Plasticized poly (vinyl chloride) (PVC) has been one of the most economically and technically important plastics materials since the 1950s. Proportions of plasticizer in commercial PVC formulations range from 15% to 50% by weight. Examples of these various formulations are present in many international museum collections, in the form of protective clothing and footwear, inflatable furniture, cable insulation, toys, medical tubing and sculpture. Many plasticized PVC formulations are designed to function for less than 20 years; this is a concern to museums where all collections should be preserved for at least 50 years. The present study outlines a strategy for prolonging the useful lifetime of plasticized PVC objects containing di (2-ethylhexyl) phthalate (DEHP).

Examination of PVC in museum collections suggested that migration, loss and chemical breakdown of plasticizer were the major mechanisms of deterioration. Model formulations were developed to represent the range of plasticized PVC objects in museum collections. The extent, rate and mechanisms of deterioration of model formulations were examined during accelerated thermal ageing in various environments, typical of those used to store and display plastics and other materials in museums. Environments included closed container, storage with silica gel, activated carbon and Ageless ® oxygen absorber, at high relative humidity, on glass and in polyethylene bags. The effect of storage in a freezer was also evaluated. In addition, two naturally aged ‘objects’, also plasticized with DEHP and exhibiting deterioration, were included in the experimental work to examine the effect of the environments on non-ideal materials.

A non-destructive analytical technique was developed using Attenuated Total Reflection Fourier Transform Infrared (ATR-FTIR) spectroscopy to quantify the concentration of DEHP at the surfaces of samples. Weight loss was used to quantify total loss of plasticizer. Changes in the distribution of DEHP were mapped using Low Vacuum Scanning Electron Microscopy (LV-SEM). Densitometry was used to quantify darkening of the PVC component of samples.

Degradation of model formulations and naturally degraded objects was inhibited by enclosure in a non-adsorbent material such as glass, containing non-agitated air. Enclosing plasticized PVC objects, whatever their level of deterioration, is inexpensive to implement, of low practical complexity and allows public accessibility to plastics objects.

Dansk resumé

Blødgjort PVC, polyvinylchlorid har - både økonomisk og teknisk set - været et af de vigtigste syntetiske materialer siden halvtredserne. Mængden af blødgører i kommercielle PVC formuleringer varierer fra 15-50 vægt%. Eksempler på disse forskellige formuleringer findes i mange internationale museumssamlinger, i form af beskyttelsesdragter og -fodtøj, oppustelige møbler, kabel isolering, legetøj, medicinaludstyr og skulpturer. De fleste formuleringer af blødgjort PVC er beregnet til at fungere i mindre end 10 år. Dette er en bekymring for de museer, hvor alle samlinger normalt forventes at holde mindst 50 år. Dette studie beskriver en strategi til at forlænge levetiden for PVC genstande, der er blødgjort med di(2-ethylhexyl) phthalat (DEHP).

Undersøgelse af PVC i museumssamlinger antydede, at migration, tab samt kemisk nedbrydning af blødgører var hovedmekanismerne i ødelæggelsen. Der blev udviklet en række modelformuleringer med det formål at repræsentere hele registeret af blødgjorte PVC genstande i museumssamlinger. Graden, hastigheden og reaktionsforløbet i nedbrydning blev undersøgt på modelprodukter under accelereret termisk ældning i forskelligartede miljøer, svarende til de forhold hvorunder man typisk opbevarer plast og andre materialer i museer. Disse forhold omfattede opbevaring i lukkede beholdere, opbevaring sammen med silicagel, med aktivt kul og med Ageless® iltabsorbere, ved høj relativ luftfugtighed, med anbringelse på glasplader og ved indpakning i polyethylenposer. Effekten af opbevaring i fryser blev også evalueret. Herudover blev to naturligt ældede "genstande", som også var blødgjort med DEHP, og som viste tegn på nedbrydning, inkluderet i det eksperimentelle arbejde, for at undersøge effekten af de forskellige miljøer på et ikke ideelt materiale.

Der blev udviklet en ikke destruktiv analysemetode baseret på Attenueret Total Reflektans Fourier Transform Infrarød spektroskopi (ATR-FTIR), med henblik på at bestemme koncentrationen af DEHP på overfladen af prøverne. Vægttab blev brugt som et kvantitativt mål for det totale tab af blødgører. Ændringer i fordelingen af DEHP blev kortlagt vha. Lav-Vakuum Scanning Elektron-Mikroskopi (LV-SEM). Densitometri blev brugt til give et kvantitativt mål for misfarvning af PVC-komponenten i prøverne.

Nedbrydning af modelformuleringerne og de naturligt ældede genstande blev hæmmet ved emballering i beholdere af ikke absorberende materiale, så som glas, indeholdende stillestående luft. At emballere PVC-genstande i glas er - uanset graden af nedbrydning - billigt og let at gennemføre. Det tillader endvidere, at publikum har adgang til plastgenstandene.

2. Introduction and background to the research project

Plastics in museums

In 1991, artists Marcel Biefer and Beat Zgraggen published the prophecy,

‘Plastic artefacts will be the most important witnesses to our time’
(Biefer and Zgraggen, 1991*)*

Plastics have had a significant influence on industrial, domestic and cultural aspects of modern life throughout the nineteenth and twentieth centuries. They represent advances in technology, illustrated by the huge range of information storage media, space suits, plastic credit cards and food containers which can be taken directly from freezer to microwave oven.

The development of plastics also reflects economic history. Restrictions on imported natural rubber to Europe during World War 2 resulted in the rapid development of alternative synthetic plastics. Between 1935 and 1945, many new polymers were introduced including polyethylene, polyamides, polymethyl methacrylate, polyurethanes, poly (vinyl chloride) (PVC), silicones, epoxies, polytetrafluoroethylene and polystyrene. Polyethylene was incorporated into radar systems while poly (vinyl chloride) replaced the limited stocks of natural rubber as cable insulation.

Public attitudes towards plastics have also changed. When the first man-made plastics formulation, cellulose nitrate, was exhibited at the Great International Exhibition in England in 1862 by Alexander Parkes, it was designed to imitate luxury materials, such as tortoiseshell and ivory, which were then in increasing demand and diminishing supply. However, this image of plastics as highly valued luxury goods faded when the colourful, post-war designs were marketed in large numbers as housewares. They developed a long-lasting image as low value, low-quality and ephemeral pieces (Russell, 1948).

The 1980s saw a change in perception of plastics from disposable materials to fashionable, highly collectable pieces with historical and technological significance. Expansion in the number of processing and fabrication techniques has allowed modern plastics to be manipulated in thin film, bulk and foam forms, and to be combined with fibres, metals and wood. Today there are 50 different basic types of plastics, included in 60,000 different plastics formulations; those based on polyolefins and poly (vinyl chloride) have highest consumption worldwide. Six new plastics materials are sent for evaluation and approval to major testing laboratories in the USA each week (Quye and Williamson,1999).

Museum objects are rarely collected for their material type but because of their origin, function, design, rarity, cultural or historical significance; plastics objects are collected for the same reasons. In this way, museums act, often unintentionally, as storage depots for both early plastics materials and the most recent experimental formulations. Some early plastics are no longer used on a commercial scale; this may be due either to concern about their flammability, toxicity or because their performance is considered inferior against today's standards. An example of this is cellulose nitrate which is highly flammable, and is therefore no longer permitted for use in public buildings or transport.

Today, all international museums and galleries possess collections which contain plastics. Plastics may be identified within collections of building materials, defence equipment, ethnography, furniture, housewares, information technology, medical equipment, modern art, photography and toys. Many incorporate metals, textiles and wood alongside plastics in their construction. In addition to the objects themselves, many of the materials used to store, transport and display them are also plastics. While museums continue their policy to collect objects which reflect everyday life and historical events, the proportion of plastics in museums will increase.

Condition of plastics collections in museums

All materials change with time, but, compared with traditional craft materials, such as stone and ceramics, plastics appear to deteriorate faster than others in museum collections. Plastics are formulated by combining materials with different chemical and physical structures, namely polymers, property modifiers and colouring materials, each of which behaves both independently and as one component in a blend.

Creators of modern art often combine several material types, selecting them by dimension, texture, colour and significance to produce their pieces, rather than by chemical compatibility. Although each material has its own degradation mechanism, it is likely that degradation of one component will influence the rate and extent of deterioration of others. The presence of metals, particularly copper, is known to accelerate the deterioration of cellulose nitrate and rubbers. In addition, many artists include recycled and discarded materials; such works may contain plastics at various levels of deterioration.

The majority of museum objects containing plastics are not new when collected, so may already exhibit deterioration. There is rarely any information about the environments in which a museum object has been used or stored during the period prior to collection. Excessive exposure to light, heat, moisture, chemicals and gaseous pollutants during that period are likely to reduce longevity.

Concern about the types of plastics present in museum collections and their condition, resulted in surveys by the British and the Victoria and Albert Museums in London in the early 1990s (Then and Oakley, 1993). Phenol- and urea-formaldehydes, cellulose acetate and nitrate, epoxy resins, polyamides, poly (vinyl chloride), polyesters, polyethylene, polymethyl methacrylate, polystyrene and polyurethanes were identified (Shashoua and Ward, 1995).

The survey of plastics objects in the British Museum collections concluded that just over one quarter (27.5%) of the 2000 objects surveyed, required no conservation treatment. Most objects (60%) were defined as being of low conservation priority, that is they were in stable condition but required some treatment such as cleaning. Less than 12% of the plastics collection were not in immediate danger, but required essential work, and the remainder (0.6%) were considered high conservation priority, displaying active deterioration. All objects in the ‘high priority’ category and most of those requiring essential work contained plasticized PVC. A similar conclusion was reached following a survey of the Modern Danish collections at the National Museum of Denmark in 1997 (Pedersen, 1999). Objects containing PVC had developed tacky surfaces, to which dust and packing materials readily adhered; shrinkage of some components was also evident.

Instability of the earliest plastics, cellulose nitrate and acetate, was recognised and expected due to their poorly stabilized formulations and because they are the oldest man-made plastics in museums. However, PVC was first developed in 1926 and still has many applications today. Research into the mechanisms by which plastics deteriorate in museum collections and appropriate preservation techniques has focused on cellulose nitrate (Hamrang, 1994 and Stewart et al, 1996) and cellulose acetates, especially since they are a major component of photographic films (Johnsen, 1997). To date, few research projects have concerned the deterioration of poly (vinyl chloride) in museum collections.

Responsibility of museums towards plastics in collections

Once plastics objects are registered in museum collections, the institution becomes responsible for their long term preservation, until the end of their useful lifetime; that point is reached, arguably, when the object ceases to have a recognisable form or meaning (Bradley, 1994). Most plastics have rather a short lifetime compared with those of traditional 'craft' materials found in museums, such as ceramics and stone. It is not usually possible to replace an early experimental formulation or original moulding, although one option may be to replace deteriorated components with their modern counterparts and display the original piece separately, to retain the significance of the object.

The definition of useful lifetime as applied to museum objects is rather different to that defined by the plastics industry. Quackenbos defined the life of a plasticized PVC film as the time in which 10% of its original weight was lost (Quackenbos, 1954). At that point, the material is considered to have changed so much in character that it has failed. Calculations based on Quackenbos’ research indicate that, depending on its formulation, lifetimes for plasticized PVC films range from 3 months to 1000 years at 25°C.

Van Oosten has observed that even if the identity of a plastics and its degradation mechanisms are known, it is still not possible to accurately estimate the ‘life expectancy’ of a plastics object in a museum. We should first establish how much deterioration is acceptable before an object shows a loss of quality. While yellowing and other changes in appearance are recognised as normal manifestations of deterioration for natural materials and are usually left untreated, the same changes in plastics objects are usually deemed unacceptable (van Oosten, 1999).

Conservation of plastics

Conservation has only been organized into a profession with recognized standards of treatment, ethical values and training programmes for around 50 years. Conservation practice has been defined by the International Institute for Conservation (International Institute for Conservation, 1987) as,

'any action taken to determine the nature or properties used in any kind of cultural holdings, or their housing, handling or treatment, any action taken to understand and control the causes of deterioration, and any action taken to better the conditions of such holdings'

It is widely acknowledged that the development of a conservation strategy for the long-term care of individual museum objects should be considered at the time of their acquisition. However, in reality, the practicalities and expenses associated with implementing such a policy are difficult for large, multidisciplinary organizations and, until recently, have been considered unnecessary for objects comprising modern materials.

In 1993, a committee of curators and conservators, representing six major museums of modern and contemporary art in the Netherlands concluded that:

- there were no generally accepted methods and criteria for solving the conservation problems of non-traditional objects of modern art.
- there was little insight into the nature and use of modern materials.
- knowledge concerning the composition and ageing of modern materials was difficult to access (Hummelen and Sillé ,1999).

Deterioration of plastics objects in museums has only been recognised as an important area worthy of research since 1991 (Grattan , 1993), while the scope of the problems surrounding the preservation of modern art has only been appreciated internationally as recently as 1998 (Hummelen and Sillé ,1999).

Conservators consider two approaches to conservation when planning treatment for any degraded object; active and passive. Active conservation treatments are those involving practical activities applied as necessary to individual objects to limit further deterioration. They include adhering broken sections, cleaning surfaces and filling missing areas to strengthen objects weakened by deterioration. Although all surveys of the condition of objects containing plastics in the United Kingdom concluded that approximately 75% of collections required cleaning, such active conservation practices are still poorly developed (Shashoua and Ward, 1995). The major cause is the sensitivity of many plastics to organic liquids, aqueous solutions and water itself, particularly if the polymer has deteriorated. The relatively low glass transition temperature of many plastics suggests that the heat generated during mechanical conservation treatments may also cause plastics surfaces to soften and flow.

Passive conservation techniques involve controlling the environments in which objects are placed during storage, display and transport, with the aim of slowing deterioration reactions. If applied successfully, such an approach can help to prolong the useful lifetime of many objects at the same time. The majority of plastics objects in museums spend their useful lifetimes in storage areas. Most importantly, passive conservation techniques are more likely to comply with the ethical practices of professional conservators, the major one of which is summarised in the code of practice (American Institute for Conservation, 1994):

‘The conservation professional must strive to select methods and materials that, to the best of current knowledge, do not adversely affect cultural property or its future examination, scientific investigation, treatment or function.’

Since there are no comprehensive guidelines defining appropriate storage environments of museum objects containing plastics as a generic group, and certainly none specifying appropriate treatments for specific types of plastics, those designed to preserve fragile organic materials such as feathers and plant fibres are commonly applied (van Oosten, 1999). These include maintaining a stable relative humidity, usually 55±3%, a temperature of 18±2ºC, light levels between 50 and 300 lux and good ventilation if the object emits gaseous products or plasticizers. There is also a recommendation that dust should be prevented from contaminating the surfaces of objects by covering with acid-free tissue paper or unbleached cotton.

To ensure that plastics objects are preserved for the enjoyment and education of future generations, it is important to specify the optimum conditions for each material and not to assume simply that the rate of various deterioration reactions by all organic materials may be inhibited by the same environment. Although the passive conservation of unplasticized PVC has been studied by the author, equivalent investigations have not been applied to plasticized material (Shashoua, 1996) . That was the objective of this project.

3. Plasticized PVC; manufacture and deterioration

Development of PVC

Baumann’s polymerisation of vinyl chloride in 1872 is regarded as the earliest documented preparation of PVC homopolymer (Tester, 1973). The first commercial interest in PVC was shown by the Carbide and Carbon Chemical Corporation, Du Pont and IG Farben, who independently filed patents in 1928. The patents referred only to vinyl chloride-vinyl acetate copolymers as opposed to the homopolymer. At that stage it was only possible to process the homopolymer in the melt state, at temperatures where high decomposition rates occurred, whereas copolymers could be processed at lower temperatures.

Effective, so-called external plasticization of the PVC homopolymer by incorporating plasticizers was first discovered around 1930, when compounding with dibutyl phthalate and other esters was found to reduce the softening point of PVC, resulting in rubber-like properties at room temperature. It was also understood that alkaline-earth metal soaps acted as heat stabilizers (Titow, 1984).

During World War 2, plasticized PVC was recognised as an effective replacement for rubber in cable insulation and sheathing, thereby helping to relieve the acute rubber shortage. Until the 1940s, Britain and the USA had been concerned largely with plasticized PVC, while in Germany, development work also concerned unplasticized PVC, a rigid material which only achieved significance in the 1960s.

The 1970s saw two events of major significance to PVC production. The oil crisis of 1973 and ‘74 caused a shortage of raw materials and fuel and an increase in prices. The discovery that vinyl chloride monomer was a carcinogen led to a change in manufacturing practice. World production today is higher than 20 million tonnes per year compared to 3 million tonnes in 1965. Annual growth rates of PVC production in recent years have been between 2 and 10%. Thus PVC is one of the most important synthetic materials.

Manufacture of PVC

PVC is a chlorinated hydrocarbon polymer. It is polymerised from the vinyl chloride monomer (VCM), which, in turn is produced from ethylene, chlorine and oxygen.

Ethylene and chlorine are reacted to produce 1,2-dichloroethane according to the reaction:

$$\mathbf{C_2H_4 + Cl_2 \longrightarrow C_2H_4Cl_2} \qquad (1)$$

The 1,2-dichloroethane is then decomposed by heating in a high temperature furnace to produce vinyl chloride and hydrogen chloride:

$$C_2H_4Cl_2 \longrightarrow C_2H_3Cl + HCl \qquad (2)$$

To make use of the hydrogen chloride produced during this reaction, it is reacted with more ethene in the presence of oxygen to produce 1,2-dichloroethane. The process is known as oxychlorination:

$$C_2H_4 + 2HCl + \tfrac{1}{2}O_2 \longrightarrow C_2H_4Cl_2 + H_2O \qquad (3)$$

The dichloroethane produced by reaction (3) is now decomposed according to reaction (2). The overall reaction may be represented as (4):

$$2C_2H_4 + Cl_2 + \tfrac{1}{2}\ O_2 \longrightarrow 2C_2H_3Cl + H_2O \qquad (4)$$

In practice, vinyl chloride is polymerised via a free radical-induced addition reaction in bulk, in suspension or emulsion (5). The molecular weight of the resultant PVC is determined by the polymerisation temperature and is little influenced by the initiator concentration. Oxygen inhibits the reaction and is excluded. The temperatures required for polymerisation range from 50-75°C.

The reaction is highly exothermic; the heat of polymerisation for PVC is 92 kJ/mol, compared with that of polystyrene (70 kJ/mol) and polymethyl methacrylate (56.5 kJ/mol)(Rodriguez, 1989). Reaction times vary from 2 hours for preparation in emulsion to 17 hours for bulk processes.

The process used to make produce more than 80% of commercial PVC polymers is suspension polymerisation (Wilson, 1995). An aqueous suspension of vinyl chloride monomer is agitated vigorously in a pressurised vessel together with protective colloids to stabilise the suspension, and buffers to control pH. The resulting PVC particles are roughly spherical and range from 50-250 µm in diameter. Polymer resulting from this process is mostly used to form products via melt processing, which requires high temperatures and mechanical work.

The commercial alternative to suspension polymerisation is emulsion polymerisation. Monomer is dispersed in an aqueous phase incorporating emulsifiers and an intiator. Polymerisation occurs at the water/monomer interface. The product has small spherical particles (0.1-2µm) with a surface layer of emulsifier. After the drying stage, these form aggregates.

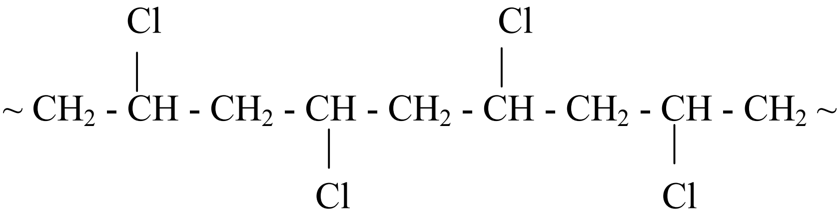
The particle size of the products from these processes, determines their end uses; PVC produced in suspension is used to make pipes, tubes and extrusions, via melt processing, whereas that produced in emulsion is more suited to preparation of dispersions, coatings, castings and foams by plastisol processing at lower temperatures.

$$\mathbf{nCH_2 = CHCl \xrightarrow{R^\bullet} (-CH_2 - CHCl-)_n} \qquad (5)$$

vinyl chloride ***poly (vinyl chloride)***

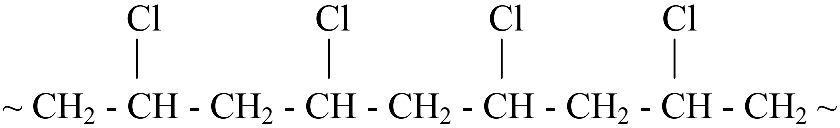
The degree of polymerisation or number of repeat units in the molecular chain, n, ranges between 500 and 1500; this corresponds to a theoretical molecular weight range of 31,000-94,000 (number average) or 100,000-200,000 (weight average). In practice, all batches contain molecules with a range of chain length.

In theory, the final polymer can take one of three isomeric conformations along the carbon backbone:



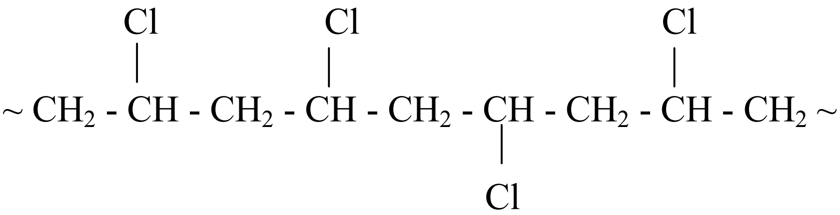
$$\sim CH_2 - \overset{\overset{Cl}{|}}{CH} - CH_2 - \underset{\underset{Cl}{|}}{CH} - CH_2 - \overset{\overset{Cl}{|}}{CH} - CH_2 - \underset{\underset{Cl}{|}}{CH} - CH_2 \sim$$

Syndiotactic (Cl atoms in alternating structure)



$$\sim CH_2 - \overset{\overset{Cl}{|}}{CH} - CH_2 - \overset{\overset{Cl}{|}}{CH} - CH_2 - \overset{\overset{Cl}{|}}{CH} - CH_2 - \overset{\overset{Cl}{|}}{CH} - CH_2 \sim$$

Isotactic (Cl atoms on same side)



$$\sim CH_2 - \overset{\overset{Cl}{|}}{CH} - CH_2 - \overset{\overset{Cl}{|}}{CH} - CH_2 - \underset{\underset{Cl}{|}}{CH} - CH_2 - \overset{\overset{Cl}{|}}{CH} - CH_2 \sim$$

Atactic (Cl atoms arranged randomly)

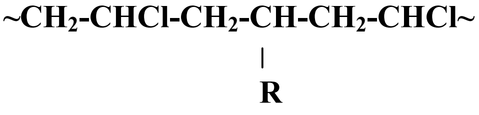
Conformation is determined mainly by the difference in Gibbs free energies between the syndiotactic and isotactic arrangements. There is a slight preference for syndiotactic conformation since it minimises the steric and electronic hindrance caused by the chlorine atom. However, this conformation is only evident at low polymerisation temperatures and at commercial production temperatures (about 60 °C). Studies using nuclear magnetic resonance techniques indicate that conventional PVC comprises about 55% syndiotactic dyads (pairs of adjacent repeating units which are syndiotactic to one another on a polymer chain), the rest being atactic in terms of dyad structure (Odian, 1991).

Commercial PVC is essentially an amorphous material, although a small amount of crystallinity is present (about 5% as measured by X-ray diffraction methods) and is attributed to the fact that that the bulky chlorine atoms do not align and pack readily. Crystallites consist of long syndiotactic sequences in the polymer chain. Despite its low percentage, crystallinity greatly influences the properties of PVC in solution and solid phases.

There has been much discussion about the nature and extent of branching in PVC. In the 1950s, Cotman reduced PVC with lithium aluminium hydride and analysed the resulting polyethylene-type product using infrared spectroscopy (Andersson, 1973). The total number of branches were determined from the ratio of methyl to methylene groups. Later, the number of end groups was used to determine branching. Various end groups may be formed during propagation or termination reactions involving the monomer and other species generated during polymerisation (Titow, 1984). It was thought that in normal commercial PVC there were up to 16 long chain branches per molecule. Recent studies, however, suggest that the existence of more than one long branch and up to 10 short branches per molecule is unlikely (Brydson, 1999). The two most probable structures for a branch junction are:

$$\sim \mathbf{CH_2\text{-}CHCl\text{-}\underset{\underset{\displaystyle R}{|}}{CH}\text{-}CHCl\text{-}CH_2\text{-}CHCl}\sim$$

and



$$\sim \mathbf{CH_2\text{-}CHCl\text{-}CH_2\text{-}\underset{\underset{\displaystyle R}{|}}{CH}\text{-}CH_2\text{-}CHCl}\sim$$

where **R** is $-\mathbf{CH_2\text{-}CHCl}\sim$ or $\mathbf{-CH_3}$

Physical properties of PVC homopolymer

The term ‘poly (vinyl chloride)’ (PVC) is commonly understood to include any plastics material or product comprising a vinyl chloride polymer or copolymer modified with additives. In this thesis, however, it refers only to the homopolymer. It’s IUPAC systematic name is poly (1-chloro-1,2-ethanediyl) but this is rarely used (Freie University of Berlin, 2001).

PVC is thermoplastic, so softens on warming. The presence of the chlorine atoms in the structure increases the attraction between chains due to C-Cl dipolar interactions, imparting great hardness and stiffness in the polymer. The glass transition temperature of commercial grade PVC is approximately 80-84°C (Titow, 1984), and the melting point around 212°C. Maximum service temperature for commercial compounds is between 65°C and 80°C in non-aggressive environments (Haward, 1973).

The polarity introduced by the presence of chlorine means that PVC is poorly soluble in non-polar solvents. It has been proposed that PVC acts as a weak proton donor and that effective solvents must behave as weak proton acceptors; examples are tetrahydrofuran and cyclohexanone. However, even good solvents are known to cause aggregation of PVC particles; they have been attributed to the presence of syndiotactic sequences (Lyngaae-Jørgensen, 1976). The high concentration of chlorine in the polymer (56.8% by weight) imparts flame retardant properties (Hirschler, 1989).

Compounding PVC

Unmodified PVC polymer is a brittle, inflexible material with rather limited commercial possibilities. Attempts to process PVC in the raw form using heat and pressure, result in severe degradation of the polymer (Nass, 1977). Hydrogen chloride is produced and rapid discolouration of the starting material from white to yellow to brown to black is observed at processing temperatures, around 150ºC.

In commercial terms, compounding PVC involves adding sufficient modifying components to the raw polymer to produce a homogeneous mixture suitable for processing and required performance at the lowest possible price. Depending on how PVC is compounded it may have rubber-like, flexible properties or have high rigidity. The formulation is determined by the future application of the fabricated PVC product, which can be electrical insulation, medical tubing, food wrap, garden hose, flooring and clothing. The formulation is also determined by the processing technique to be employed.

Modifiers for polymers may be classified into the following groups:

- Plasticizers
- Stabilizers
- Lubricants
- Impact modifiers
- Processing aid polymers
- Fillers
- Colouring agents
- Miscellaneous (antistatic agents, foaming agents, flame- retardants, fungicides and perfumes)

Table 3.1 Modifiers for PVC polymer

modifier	**major function**	**how achieved**	**example**
plasticizer	soften PVC reduce Tg	separates PVC chains	phthalate esters aliphatic diesters epoxidzed oils phosphate esters polyesters
stabilizer	minimise or eliminate degrading effects of heat, light or oxygen on PVC	react with degradation product (HCl)	tin mercaptides barium-cadmium salts of fatty acids lead salts alkyl benzenes epoxidized soya bean oil
lubricant	prevent adhesion of compound to processing equipment	sweats out to form a film between PVC and equipment	calcium stearate normal and dibasic lead stearate
impact modifier	reduce brittleness	impedes crack development	acrylonitrile-butadiene-styrene ethylene-vinyl acetate copolymer
processing aid	ensure uniform flow and good surface finish	affect melt viscosity of polymer	acrylates acrylonitrile-butadiene-styrene
filler	opacify compound increase hardness reduce cost	changes refractive index and reflective properties adds bulk to compound	calcium carbonate magnesium carbonate barium sulphate

Source of data (Titow, 1984 and Brydson, 1999)

There is some overlap between the properties and actions of all polymer modifiers (Table 3.1). For example, plasticizers may also act as impact modifiers and lubricants. Conversely, a commercial impact modifier or lubricant may act as a plasticizer once incorporated into a PVC formulation.

Compounded PVC may further be divided into two main types, defined by the properties imparted by additives, namely unplasticized (uPVC) or rigid PVC, containing none or little plasticizer respectively, and plasticized (pPVC), flexible or soft PVC. Today, uPVC accounts for about two thirds of total use and plasticized PVC for one third. Forty years ago, the proportions were almost reversed, with plasticized PVC taking priority.

Plasticizers

Plasticizers are the major modifier for PVC formulations in terms of percentage weight (between 15 and 50%) and, therefore, have the greatest influence on the properties and behaviour of the compounded PVC (Table 3.2).

A plasticizer is a material incorporated into a polymer or polymer mixture to increase its workability and its flexibility or elongation (Wilson, 1995). Plasticizers are essentially non-volatile solvents, with solubility parameters close to that of the polymer and a molecular weight of at least 300. Plasticizers are typically high boiling, oily, organic liquids, usually esters. Addition of plasticizer to a PVC polymer has two main functions; to assist in the processing stage by reducing the viscosity and melting temperature, and to modify the final product by softening it.

Table 3.2 Effect of plasticizer DEHP (di (2-ethylhexyl) phthalate) concentration on physical properties of PVC moulded at 178°C and under pressure for 5 minutes

DEHP (per hundred parts PVC, phr)	**DEHP (% by weight based on PVC plus DEHP)**	**100% modulus [1] (N/mm^2)**	**Elongation at break [1] (%)**	**Low temperature flex point[2] (°C)**
30	23.1	20.2	270	+ 3
40	28.6	14.7	300	-10
50	33.3	10.2	325	-22
60	37.5	7.0	370	-30
80	44.4	3.7	420	-44
100	50.0	2.4	430	-51

From (Wilson, 1995)

[1] *As determined using BS 2782 (1970) Method 301E*

[2] *Lowest temperature at which a standard strip can be deflected through an angle of 200° under fixed torque without failing (BS2782:Part 1: Method 150B:1976)*

Of the one million tonnes of plasticizers used annually in Europe, approximately 90% comprise phthalate esters; the most frequently used are di (2-ethylhexyl) phthalate (DEHP), di-isononyl phthalate (DINP) and di-isodecyl phthalate (DIDP). The largest single product used as a general purpose plasticizer worldwide is DEHP and it has set the standard for performance to price relationships since the 1950s. DEHP is unique among phthalate plasticizers for PVC because it has a single chemical component, di (2-ethylhexyl) phthalate. The IUPAC systematic name for DEHP is 1,2-benzenedicarboxylic acid bis (2-ethylhexyl) ester, but it is seldom used (Freie University of Berlin, 2001). In the absence of special processing or service requirements, the formulator normally considers DEHP first. Several phthalates including DEHP are known as primary plasticizers due to their documented high compatibility with PVC polymers (Titow, 1984). The behaviour of DEHP in compounded PVC was the central focus of this research.

Manufacture of DEHP

DEHP is an ester manufactured from phthalic acid and 2-ethylhexanol. Phthalic anhydride is produced by catalytic oxidation of either naphthalene from coal tar distillation or, more commonly today, by oxidation of orthoxylene. 2-ethylhexanol is manufactured from propylene.

Formation of the monoalkyl phthalate occurs rapidly at relatively low temperature by ring opening of phthalic anhydride (Figure 3.1). Conversion to the diester is slower, requires heating to 140-150°C and the presence of a catalyst (Wilson, 1995). The use of a catalyst reduces reaction temperature, thereby minimising loss of the volatile alcohol. Sulphuric acid and para-toluenesulphonic acid are the most commonly used catalysts. Equilibrium is driven towards complete phthalate formation by removal of water, usually under vacuum. Excess 2-ethylhexanol is introduced to ensure complete conversion of phthalic anhydride, and recycled after esterification is completed. After purification, commercial grades of DEHP contain less than 0.1% of unreacted 2-ethylhexanol.

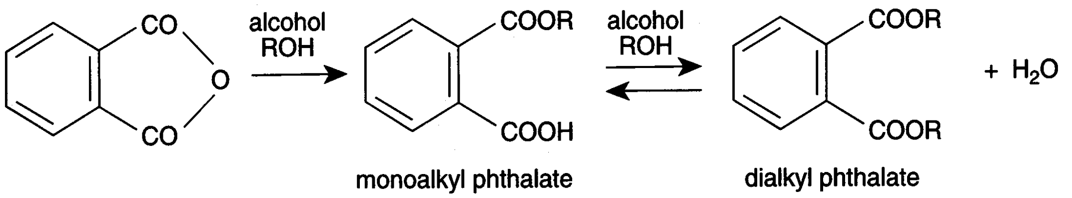


Figure 3.1 Manufacture of phthalate plasticizers. 2-ethyl hexanol is the alcohol used to prepare di (2-ethylhexyl) phthalate DEHP (From Wilson, 1995)

Manufacture of plasticized PVC

The stages of the plasticization process involve mechanically milling the solid, agglomerated (large particle size) polymer with sufficient liquid plasticizer to reduce the particle size, increase the surface area to volume ratio and, thereby, inhibit reagglomeration of the polymer particles. During this process, plasticizer molecules are effectively dispersed throughout the PVC, and attach themselves to the surfaces of the polymer particles by physisorption. A Van der Waals interaction takes place between the plasticizer and polymer particles. Such interactions have enthalpy values in the order of 20 kJ/ mol, approximately ten times lower than such values for covalent, chemical bonds.

Next, the remaining plasticizer, and other modifiers are added. Plasticizer diffuses within particles. The plasticizer is probably present as clusters of molecules between bundles of polymer segments or molecules. The PVC molecules are no longer held rigidly together, but are in a rubbery state dispersed by the plasticizer molecules. At this stage it is important that the plasticizer is evenly dispersed to perform its intended function in the final product. Heat is introduced to achieve the high activation energy required for this process.

On a molecular level, plasticization is the weakening or selective breaking of bonds between molecules, while leaving others intact, to increase intermolecular space, known as free volume. It is this increased space which allows room for changes in shape, flexing or moulding of the final material. The PVC polymer is semi-crystalline and may be thought of as comprising small areas of order, crystallites, among disordered or amorphous areas of molecules. Areas containing a high proportion of crystallites tend to make the polymer rigid, while amorphous areas tend to induce flexibility. It has been shown using infrared spectroscopy, that when plasticizer is incorporated into the PVC polymer, it solvates the amorphous chain segments, but not the crystalline ones (Tabb and Koenig, 1975).

When a small amount of plasticizer is incorporated into PVC, polymer chains rearrange to become more ordered and to increase the proportion of crystallites; this has been detected by X-ray diffraction (Horsley, 1957). The few plasticizer molecules present tend to form hydrogen bonds between the oxygen in the plasticizer and hydrogen in the PVC, leaving insufficient numbers available to fill the intermolecular space-an activity which, in other circumstances, increases softness of the mixture. Instead the poorly plasticized formulation becomes more rigid and has higher tensile strength, poorer impact resistance and elongation than the unplasticized PVC polymer itself. This phenomenon is known as antiplastization. When the amount of plasticizer is increased, the opportunity for an increase in crystallinity is still present, but the additional plasticizer occupies the amorphous areas introducing softness and flexibility to the whole.

There is a plasticization threshold concentration above which the softening effects of plasticizers are manifested, and below which antiplasticization limits such developments. The threshold limit for a particular polymer with specified molecular weight, varies with the plasticizer type, but is around 15% by weight for DEHP in PVC (Ghersa, 1958). As a result, there are no commercial plasticized PVC compounds based on DEHP concentrations lower than 15%.

According to the major texts concerning PVC technology, DEHP is completely compatible with PVC, but as a solvent it is very poor. It will dissolve only about 2% PVC at room temperature without gelling (Sears and Darby, 1982). This is partly due to the presence of areas of PVC-PVC polymer chain interaction which inhibit the possibility of solution as opposed to plasticization.

In PVC technology, two forms of polymer dispersed in plasticizer may be produced; plastisol and dry blend. The plastisol is a pourable, creamy dispersion of finely divided PVC in a liquid plasticizer. The dry blend is a blend of powdered PVC polymer and liquid plasticizer in which the plasticizer has been absorbed until a pourable powder is formed. Both forms may be converted to plasticized PVC after heating or fusion and cooling. Typical applications for formulations based on DEHP are shown in Table 3.3.

Table 3.3 Typical applications for plasticized PVC formulations

DEHP (per hundred parts PVC, phr)	**DEHP (% by weight based on PVC and DEHP)**	**application**
20	16.7	vinyl flooring [1]
30	23.1	upholstery cover [2]
40	28.6	document folder [1]
50	33.3	garden water hose [3]
60	37.5	electrical cable sheath [3]
80	44.4	shoe sole [2]
100	50.0	rubber (wellington) boots [2]

[1] *(Wickson, 1993)* [2] *(Wilson, 1995)* [3] *(Brydson, 1999)*

Lifetime of plasticized PVC

The useful lifetime of plasticized PVC depends on its ability to resist degradation in the conditions prevalent at the time of manufacture and in its environment of use. Changes in any one of the components of the formulation, that is polymer, plasticizer or one of the other modifiers , will affect the whole composition and may influence the lifetime of the whole. For example, hydrogen chloride, formed as a result of thermal or photodegradation of PVC can destroy aluminium pigments in a uPVC window frame. Such changes may occur rapidly, for example as a result of high processing temperatures or over longer periods during use (Table 3.4).

Degradation of the two major components of all plasticized PVC materials, the polymer and plasticizer, will be considered independently first and then in combination.

Table 3.4: Major categories of use of PVC in Europe (1999)

category	**example of application**	**percentage**	**average lifetime (years)**
building	uPVCwindow frames	57	10-50
packaging	film and sheet	9	1
furniture	fake leather upholstery	1	17
household appliances	PVC tubing	18	11
electric and electronic	cable insulation	7	21
automotive	steering wheel cover	7	12
others	blood bags	1	2-10

Source: European Union Commission, 2000

Lifetime of polymer component

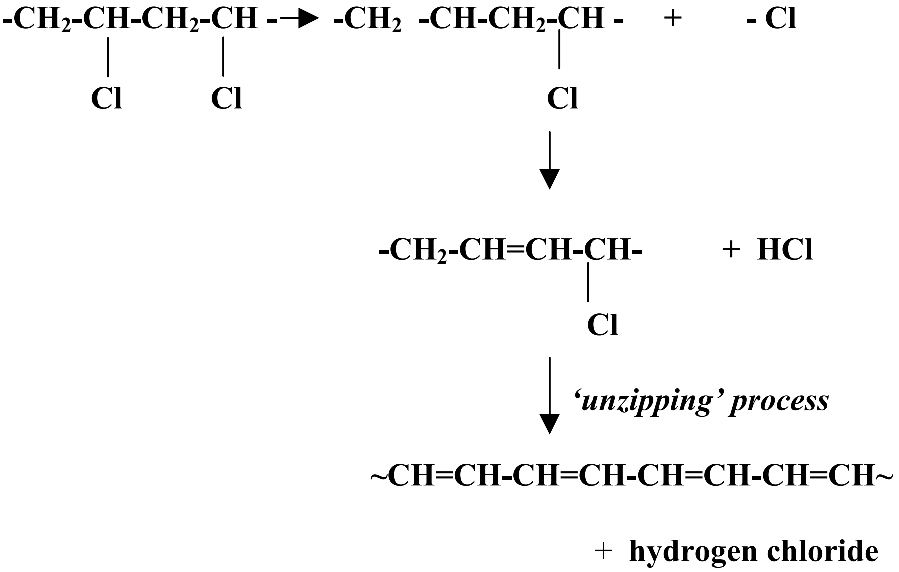
PVC is susceptible to degradation when exposed to heat and light; degradation is more rapid and severe in the presence of oxygen. The effects of ultraviolet light and weathering are important considerations for the performance of building materials, but less relevant for museum objects, so will not be considered further here.

Since heating to temperatures higher than 70ºC affects its properties, standard processing temperatures (150-200ºC) would render PVC useless if stabilizers and inhibitors were not present in the formulation. The activation energy for thermal degradation of the PVC polymer is approximately 83.6kJ/ mol ; this is low compared with that for polyethylene (192.5kJ/mol), polystyrene (230.1kJ/ mol) and polypropylene (272kJ/ mol) (Rice and Adam, 1977).

The vulnerability of PVC to heat is due only to its structural irregularities, which include carbon-carbon double bonds at chain ends, tertiary chlorides, oxygen-containing structures and catalyst residues from the polymerisation process. These have lower thermal stability than the linked vinyl chloride units and, therefore, act as initiation sites for degradation even at very low concentrations (Andersson, 1973). Other things being equal, thermal stability is greater for PVC manufactured by the bulk process, than that produced by suspension or emulsion due to traces of surface-active agents in the latter.

The degradation mechanism by which thermal degradation of PVC takes place is complex. In general, it comprises one major reaction; the evolution of hydrogen chloride (dehydrochlorination process). In addition, cross-linking and chain scission reactions affect the physical properties of the degraded PVC. Cross-linking results in high molecular weight, stiff polymers, while chain scission reduces the molecular weight, thereby increasing solubility.

It is usually assumed that dehydrochlorination starts at imperfections in the PVC structure and that the breaking of the first C-Cl bond may follow either a free radical or ionic mechanism. The mechanism is still not completely established (Iván, 2001). Loss of a chlorine atom is followed almost immediately by abstraction of a hydrogen atom and a shift of electrons in the polymer to form a double bond. The next chlorine becomes allylic, highly reactive and is readily removed. Without assuming that either free- radical or ionic mechanisms are followed, the process may be represented as in Figure 3.2:



$$\mathrm{-CH_2-\underset{\substack{|\\ Cl}}{CH}-CH_2-\underset{\substack{|\\ Cl}}{CH}-} \rightarrow \mathrm{-CH_2\ -CH-CH_2-\underset{\substack{|\\ Cl}}{CH}-} \quad + \quad \mathrm{-Cl}$$

$$\downarrow$$

$$\mathrm{-CH_2-CH=CH-\underset{\substack{|\\ Cl}}{CH}-} \quad + \ \mathrm{HCl}$$

$$\downarrow \ \textit{'unzipping' process}$$

$$\mathrm{\sim CH=CH-CH=CH-CH=CH-CH=CH\sim}$$

$$+ \ \textbf{hydrogen chloride}$$

Figure 3.2 Dehydrochlorination reaction of PVC leading to 'unzipping'

This leads to the progressive 'unzipping' of neighbouring chlorine and hydrogen atoms to form a conjugated polyene system with alternate single and double carbon bonds, accompanied by the formation of hydrogen chloride. As the conjugated polyene system develops, the polymer begins to absorb radiation in the ultraviolet part of the spectrum. After between 7 and 11 repeat units have formed, absorption shifts to longer wavelengths until it is absorbing in the violet, blue and green parts of the spectrum. Each absorption maximum has been found to correspond to a specific polyene length. The rate of degradation can be followed using colour changes from white to yellow to orange to red, brown and, ultimately black. Dehydrochlorination is an autocatalytic reaction, that is, if the hydrogen chloride produced is not removed from the environment surrounding PVC, dehydrochlorination continues at an accelerated rate (Brydson, 1999).

In the absence of oxygen, thermal degradation occurs slowly, although increasing temperatures promote cross- linking. Such reactions terminate the growing polyene sequence, thus limiting the extent of discolouration. When oxygen is present, thermal degradation occurs more rapidly and the degradation mechanisms become more complex (Andersson, 1973). Dehydrochlorination is greatly enhanced in the presence of oxygen, particularly at the sites of double bonds. Acids, ketones and carbon-carbon unsaturation are formed in addition to hydrogen and water. Chain scission occurs more readily than cross-linking between two adjacent chains.

The balance between all the degradation reactions involved, changes with temperature, time, energy available and the presence of other materials. As a result, the properties of thermally degraded PVC vary with environmental conditions.

Influence of chemical stability on lifetime of DEHP

As esters, phthalate plasticizers are susceptible to hydrolysis when exposed to strongly acidic or alkaline environments**.** At temperatures higher than 200°C, fragmentation of the plasticizer molecule begins to occur. Boiling DEHP (386°C) for 1 hour results in a 30% decomposition mainly into phthalic anhydride, 2-ethyl hex-1-ene and 2-ethylhexanol in the approximate molar ratio 1:1:1 (Wilson, 1995). Acid catalysis lowers the temperature of decomposition and alters its course, causing the formation of phthalic acid instead of phthalic anhydride plus an additional mole of 2-ethyl hex-1-ene instead of 2-ethylhexanol (Figure 3.3).

Alkaline hydrolysis causes the acid produced to be converted to the salt and the reaction proceeds to completion, that is saponification. Such sources of alkali include concrete and drying agents including calcium oxide, materials which are not so commonly found together with PVC in museum collections.

Pyrolysis GC-MS of DEHP under vacuum up to 500° C, has identified crystals of phthalic anhydride, benzene, toluene and benzaldehyde from the scission of the CO-O bond (McNeill and Memetea, 1994). Pyrolysis in air also yields products formed by dehydrocyclization, including styrene, naphthalene and methyl naphthalene.

Oxygen attack on alkyl groups in the DEHP molecule also results in the formation of phthalic acid. There are two identical tertiary C-H positions which are susceptible to oxidation (Figure 3.4). Such oxidative reactions are expected to occur both at ambient and processing temperatures (200ºC), forming phthalic acid as the main reaction product.

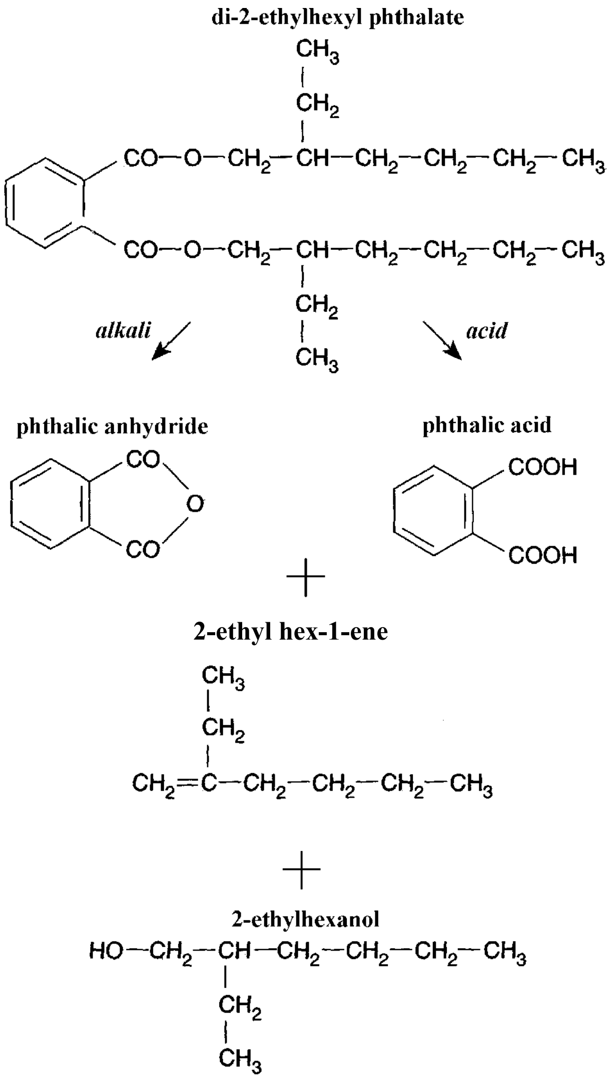


Figure 3.3 Hydrolytic breakdown of DEHP

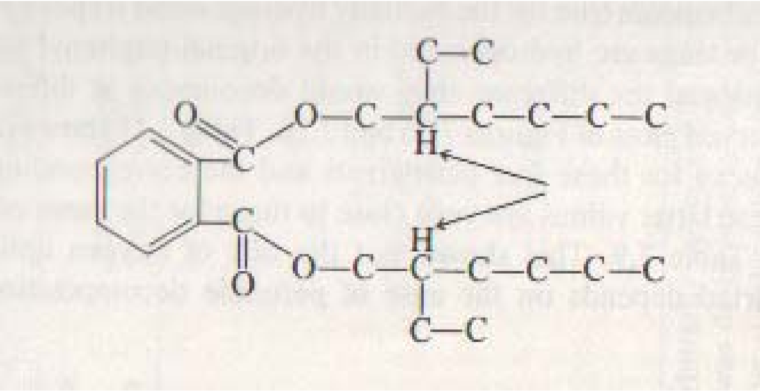


Figure 3.4 Two equivalent tertiary C-H positions in the DEHP molecule are vulnerable to oxidation (From Sears and Darby, 1982)

The rate of oxidation is controlled by the rate of diffusion of oxygen to the site of reaction. As a result, it is most likely to occur first at the air/surface interfaces of a plasticized PVC sheet or object. Oxidation is considered to be a chain reaction consisting of three basic stages-initiation, chain propagation and chain termination (Figure 3.5). There is no single route by which each stage occurs, but there is a slow induction period, followed by an autocatalytic, fast oxidation stage proceeded by a slowing of the rate (Sears and Darby, 1982).

Initiation: **Initiator $\rightarrow$ free radicals**

Chain propagation: $\mathbf{R\bullet + O_2 \rightarrow RO_2\bullet}$

$\mathbf{RO_2\bullet + RH \rightarrow ROOH + R\bullet}$

Chain termination: $\mathbf{RO_2\bullet + RO_2\bullet \rightarrow}$

$\mathbf{RO_2\bullet + R\bullet \rightarrow}$ **nonradical products**

$\mathbf{R\bullet + R\bullet \rightarrow}$

RH refers to **DEHP** at tertiary **C-H** position
$\mathbf{R\bullet}$ is the free radical derived from **RH** after loss of hydrogen
ROOH is the hydroperoxide
$\mathbf{RO_2\bullet}$ is the peroxy radical

Figure 3.5 Mechanism of oxidation for DEHP

Oxidation of DEHP may not be detected visually until it reaches an advanced stage and the peroxy radicals begin to decay, causing discolouration to occur and unpleasant odours to develop, a process known as latent degradation. This is usually attributed to overheating during processing and poor formulating; absence of sufficient antioxidant is the most common cause.

Influence of chemical stability on lifetime of plasticized PVC compounds

The individual effects of the polymer and plasticizer components on the thermal stability of compounded PVC are difficult to determine. There are two options; either the PVC component begins to deteriorate and destabilizes the plasticizer or vice versa.

Thermal analytical studies in an oxygen-free atmosphere with formulations containing various concentrations of DEHP, have shown that decomposition of PVC happens before that of the plasticizer. At PVC concentrations higher than 16%, plasticizer no longer boils off alone at 400°C, but at around 360°C, since its degradation has been combined with that of PVC (Dunn and Ennis, 1970). Pure DEHP produced a peak at 300°C under the conditions of the analysis. Analysis of the volatilized decomposition products identified phthalic anhydride and octenes in the gas phase.

Further evidence for the influence of polymer on the rate of degradation of plasticizer, comes from the observation that the thermal degradation products of DEHP change from phthalic anhydride and 2-ethylhexanol, produced when DEHP degrades alone, to the free acid plus an additional mole of 2-ethyl hex-1-ene when heating the plasticizer with 5% PVC for 40 hours at 170°C. The acidic conditions required are likely to be provided by hydrogen chloride, the main degradation product of PVC (Wilson, 1995).

Considering the influence of plasticizers on the degradation of PVC, it has been proposed that the formation of free radicals during oxidation of DEHP may attack PVC chains and initiate dehydrochlorination (Wilson, 1995). However there is insufficient published evidence to support this proposal.

Addition of phthalate plasticizers has been shown to reduce the rate of dehydrochlorination by PVC at temperatures between ambient and 300°C, by inhibiting the growth of polyene sequences. Ester groups in DEHP solvate the labile groups of the polymer chain which are responsible for the instablity, thus avoiding double bond formation (Beltran and Marcilla, 1997).

Physical influences on the lifetime of plasticized PVC compounds

The instability of plasticized PVC is frequently manifested as migration of the plasticizer from the bulk phase to the outermost surface layer. From there, plasticizer evaporates at a rate dependant on the vapour pressure of the particular plasticizer. Such instability is manifested by a tacky feel to the plastic and increasing embrittlement of the bulk plastic as degradation proceeds. This process was sufficiently important to merit extensive investigation by the Bakelite company as early as 1954 (Quackenbos, 1954). In the museum environment, instability of plasticized PVC objects may be detected as early as 10 years after collection, although it is highly dependent on the previous history and function of the piece.

The ideal plasticizer would exhibit zero loss from PVC and would remain chemically unchanged despite prolonged exposure to heat, light, aggressive chemicals, micro-organisms and absorbent materials. Since plasticizer molecules are not chemically bound to the polymer, but held only by long-range, weak forces, they move from their original position quite readily even at low temperatures. During the processing stage, temperatures, usually above 150°C, are sufficiently high to break the weak bonds and increase mobility of both polymer molecules and plasticizer.

The phenomenon of plasticizer loss involves both thermodynamic and kinetic factors. Thermodynamics concerns the strength of interaction of the plasticizer with

PVC, compared to its compatibility with the medium into which it is moving. Such media include air, organic liquids such as oils, dry foods and other plastics (Sears and Darby, 1982). Kinetics concerns the rate at which the plasticizer migrates to the surface of the PVC and then moves from the surface to the absorbent medium.

From a thermodynamic viewpoint, the free energy of mixing polymer and plasticizer contains enthalpic and entropic components. To describe the phase behaviour of the system, the enthalpic and entropic contributions must be related to the molecular characteristics of the components. By estimating the entropy and enthalpy of mixing PVC and DEHP, the free energy of mixing, $\Delta\mathbf{G}_{\mathbf{mix}}$ at absolute temperature **T** may be derived:

$$\Delta\mathbf{G}_{\mathbf{mix}} = \Delta\mathbf{H}_{\mathbf{mix}} - \mathbf{T}\Delta\mathbf{S}_{\mathbf{mix}}$$

The entropic contribution, $\Delta\mathbf{S}_{\mathbf{mix}}$, always favours mixing, though it is less favourable for higher molecular weight components, while the enthalpy of mixing, $\Delta\mathbf{H}_{\mathbf{mix}}$ **,** is independent of the polymer's molecular weight. When the enthalpy for a mixing system is unfavourable, and endothermic, the entropy must be sufficiently large to give an overall negative free energy of mixing. As the molecular weights of the components increase, a point is reached where the entropy of the system is so low that the enthalpic contribution prevails and phase separation results. However, when the enthalpy of mixing is favourable, and exothermic, the conditions for miscibility are always satisfied (Garbassie et al, 1998).

Considering the mixtures of plasticizer and polymer as semi-dilute or concentrated solutions, the simple Flory-Huggins model can be applied. Due to its relative simplicity, the Flory-Huggins model has been used extensively in research and industry to predict the compatibility between polymers and plasticizers or solvents and thus select the best matches.

The Flory-Huggins parameter χ is a dimensionless measure of the strength of the interaction between, in this case, the PVC molecules and the plasticizer molecules. Lists of parameters may be found in handbooks (Barton, 1983) . The basic premise for the Flory-Huggins theory is that the polymer molecule behaves like a freely jointed chain composed of discrete segments which, together with the plasticizer molecules, occupy sites on a lattice (Flory, 1953). Each lattice site must be occupied by either a polymer chain segment or a plasticizer molecule; there are no vacancies. In addition, adjacent segments of the polymer occupy adjoining lattice sites.

The Flory-Huggins parameter is derived from the enthalpy of mixing and may be calculated from the following equation (Foss and Shaw, 1985):

$\chi = (z.\ \Delta w_{12.}\ x_1)\ /\ kT$ where

z is a lattice coordination number

w_{12} is the energy of formation of a polymer segment /solvent interaction

x_1 is the number of sites occupied by a solvent molecule,

k is the Boltzmann constant and T is absolute temperature

The interaction parameter is lower or equal to 0.5 if a polymer is compatible with a plasticizer in all proportions, values greater than 0.5 indicate poor solvency and the possibility of separation of the two materials.

Foss and Shaw applied gas-liquid chromatography to the analysis of plasticizer/polymer thermodynamics. The polymer matrix of interest is coated from solution onto a suitable support. A gas chromatography column is then filled with the coated support. The column is installed in a normal gas chromatograph and the plasticizer of interest is injected. The Flory-Huggins interaction parameter is related to the retention time of the plasticizer on the column.

This technique has also been applied to systems involving two-component stationary phases, where the interaction of interest is between the two stationary components. The components studied include polymer/plasticizer systems. The purpose of inverse Gas-Liquid chromatography (GLC), as it is known, is to determine the interaction between the components of a mixed stationary phase from the interaction of a volatile probe molecule or solvent, and the stationary phase. It is also necessary to know the individual interaction parameters for the probe. They may be determined from GLC experiments on columns coated with pure components. Although this technique has the disadvantage that the interaction parameter for he polymer/plasticizer is dependent on the probe solvent used, the advantages of being able to measure the interaction parameter as a function of concentration and temperature are significant.

Although only one study using inverse Gas-Liquid chromatography to evaluate the Flory-Huggins parameters of PVC-plasticizer systems has clearly stated that the compatibility of PVC and phthalate plasticizers is dependent on the concentration of plasticizer, other researchers have presented results which may be interpreted in that way (Kondyli et al, 1990). Su et al. calculated that the Flory-Huggins parameter is high up to plasticizer volume loadings of about 25% (Su et al, 1976), from 25% to around 60% (by volume) of phthalate, the interaction parameter rises and becomes greater than 0.5 above 60%. At such concentrations of phthalate, it may be concluded that much of the plasticizer is ‘mobile’, that is in contact with other phthalate molecules, rather than ‘bound’ or in contact with the surfaces of PVC molecules. Such results may indicate thermodynamic incompatibility at high phthalate concentrations, however the temperatures used were higher than ambient (110-130°C).

As oxidation occurs in plasticized PVC, the compatibility of both polymer and plasticizer change. Interaction parameters, such as solubility parameters increase as polar degradation products are formed, and at some point polymer and plasticizer may become incompatible. This is especially likely if compatibility was borderline in the unaged system.

It costs a polymer system some energy to produce a new surface, such as that made by migrating plasticizer on solid PVC. The reason for this is that space must be created for the new surface and molecules must either be moved from their positions in the bulk phase to the surface (usually a high energy-consuming and, therefore, undesirable prospect in the solid phase) or reoriented to assume a new equilibrium position. The intermolecular forces experienced by surface molecules compared with those acting on them when they are part of the bulk material lead to an increase in free energy.

The underlying principle for all discussions concerning thermodynamics of surfaces is that a surface will always attempt to achieve the lowest interfacial energy. If a polymer system contains more than one component, the one which minimises the interfacial energy tends to migrate to the surface and concentrate there. The degree to which this desirable situation can be realised depends on the molecular mobility exhibited by the polymer. Increasing the temperature of the polymer system above the glass transition temperature, melting the polymer, dissolving the polymer and adding plasticizers can be used to promote molecular mobility and stabilise the surface structure from a thermodynamic viewpoint. If the mobility is too low, energetically less favourable structures can be frozen into place.

The most common processes by which plasticizer is lost from PVC are volatilization, extraction and migration:

Volatilization

During volatilization, plasticizer is lost from the air/polymer interface. The two mechanisms controlling the rate of volatile loss of a plasticizer from PVC are diffusion to the surface and evaporation from the surface. Under different conditions either one of these can be the rate-determining step, but for most normal uses of plasticized PVC, it is the rate at which evaporation occurs which determines the speed and extent of plasticizer loss. Evaporation rate is dependent on the vapour pressure in the environment surrounding the surface.

Studies on PVC have shown that within certain limits, the vapour pressure is independent of plasticizer concentration. If the plasticizer concentration is higher than the antiplasticization range, the plasticizer is readily available for evaporation so that the surface becomes the controlling factor. Under equal conditions, percentage plasticizer lost is inversely proportional to film thickness for at least up to 50% plasticizer loss (Small, 1947). The vapour pressure for phthalate plasticizers between 80°C and 250°C is shown in Table 3.5. There is little reliable data available for vapour pressure of plasticizers at ambient temperatures or for blended plasticizer systems. It suggests that plasticizer loss approximately doubles for every 10°C increase in temperature (Wilson, 1995).

Vapour pressure values have been extrapolated back to ambient temperatures to predict service lives of plasticized formulations, based on Quackenbos' assumption that a PVC film had failed when it has lost 10% of its mass (25-30% of the plasticizer content). Graham calculated service lives for compounds plasticized with DEHP of 4.2 years at 40 °C and 1150 years at 0°C (Quackenbos, 1947). Any effects due to chemical degradation of DEHP and PVC were not considered in these calculations.

Table 3.5 Vapour pressure of plasticizers at various temperatures

Vapour pressure (Pa)

Plasticizer	**80°C**	**100°C**	**140°C**	**180°C**	**250°C**
di-n-butyl phthalate	2.0	8.2	87.0	608.0	8667.0
di-ethylhexyl phthalate		0.1	3.9	57.1	2075.0
di-octyl adipate		0.1	2.3	28.2	969.7

Source of data(Wilson, 1995)

Diffusion becomes the rate determining step when conditions encourage rapid removal of vapour from a surface. Such conditions include vacuum or rapid air flow. The rate of diffusion is related to the plasticizer's molecular size and shape and to the permeability of the PVC. Permeability is strongly influenced by plasticizer level and diffusion is slower through a lightly plasticized formulation than through the more open structure imparted by high plasticizer levels.

However, the rate of diffusion through a new sample of PVC containing, say 30% by weight plasticizer compared with a sample which was formulated with, say 40% by weight and has, with time, lost 10% plasticizer may be different. Although both samples now contain equal amounts of plasticizer, the structure of the degraded sample may be more open, and contain more voids than the new one. In addition, polymer or a mixture of PVC and plasticizer may have migrated to partially fill any voids left by the lost plasticizer.

If the plastics material has a completely homogeneous physical structure, then volatile loss as controlled by evaporation is linear with time and independent of plasticizer content in a constant environment. The rate of diffusion may, but does not always obey Fick's first law of diffusion, which states that the loss of plasticizer particles is linear with the square root of time. Usually Fick's law applies to polymers possessing a flexible rather than a stiff backbone (Vergnaud, 1974).

Windscreen fogging is the well-known phenomenon by which a thin film of plasticizer forms on the interior glass surfaces of a new car, reducing their transparency. There have been many suggestions for the cause, but a major contributing factor is the manufacture of seat coverings, dashboards and crashpad skin from plasticized PVC. The stationary car represents a closed system in which air exchange is minimal. The internal temperature may be as high as 100°C on a warm day-sufficient to promote evaporation of the volatile phthalate plasticizers commonly used for such low-cost applications (Pugh, 1965).

Initially, the concentration of plasticizer in the air space of the car is very low, plasticizer diffuses out of the furnishings rapidly and into the air. When the plasticizer vapour saturates the air in the car, it condenses on the clean glass and forms droplets (Howick, 1995). Such drops scatter light causing the appearance of fogging. If the PVC surfaces are wiped or washed to remove exuded plasticizer, additional plasticizer will diffuse to the surface to redress the concentration difference.

In addition, since the concentration of plasticizer in the air of the car is now high, and heat is present, the possibility exists that the plasticizer will diffuse from one material into another containing a lower concentration, or zero concentration of plasticizer. In this way, some surfaces within the car may gain plasticizer while others are losing it.

Extraction

During extraction, plasticizer is lost from a liquid/ polymer interface. Immersion, application of a liquid to a surface or exposure to high levels of atmospheric moisture can cause loss of plasticizer from a PVC formulation. Most plasticizers for PVC are hydrophobic and, as such, have low solubility in water (between 0.1-1.0%). However, association between the polymer and water molecules can displace plasticizer molecules, particularly the more hydrophobic types. The displaced plasticizer forms an oily film on the surface.

If surfactants are present in the water, they disperse and remove the plasticizer film, encouraging further extraction by diffusion. With very high concentrations of surfactant, removal from the interface may become faster than diffusion through the PVC . In this case, the process becomes diffusion controlled.

Migration

During migration, plasticizers are removed from PVC by contact with any absorbent material. It is also necessary for some pressure to be applied to both plastics and absorbent in order to encourage intimate contact between the two surfaces and promote movement of the liquid plasticizer from its original position. The pressure may originate from an external source or be an inbuilt stress connected to the function of the plastics. In the case of telephone cables, the PVC insulation is stressed during production and supported by the copper core. The PVC makes contact with itself at many points (Wilson, 1995). Low molecular weight plasticizers are likely to be removed when subjected to pressure. Migration may cause softening, staining and loss of mechanical performance for the adsorbent.

Concern for consumer safety has promoted investigations into migration of plasticizers from PVC packaging into foods. Diffusion of DEHP from the bulk of a PVC packaging film to its surface was identified as the rate-determining step during examination of plasticizer migration into ground meat (Kondyli et al, 1992). The rate of migration was dependent on temperature; the meat adsorbed almost ten times more plasticizer if stored in a fridge (4° C) than a freezer (-20 °C) for the same period.

Agitation of the adsorbing medium increased the rate of loss of DEHP. This study was also interesting because of the complex procedure used to quantify migrating plasticizer. DEHP was extracted, saponified and extracted in alcohol before gas chromatography was used to analyse it.

Application of mechanisms of plasticizer loss to the museum environment

In practice, all three physical processes by which plasticizers are lost may occur in the museum environment. Consider the situation inside a fairly well sealed, glass museum showcase or storage enclosure containing various objects including some with plasticized PVC components. As the lighting in the museum or storage area is focused on or near to the closed system, the contained air is heated. As a result, evaporation of the plasticizer is likely to occur from the plasticized PVC. Diffusion from the surfaces containing higher concentrations of plasticizer, to those which contain none or lower levels is energetically favourable. By this mechanism, plasticizer moves from the plasticized PVC into the surrounding air space and onto the surfaces of other objects which have a lower concentration of plasticizer than the original. As the concentration of plasticizer decreases at the surface, more plasticizer diffuses through the original object to redress the concentration balance.

The loss of plasticizer by migration may be observed in the museum environment when an absorbant material, such as cellulosic or bonded polyester tissue is used to cover the surfaces of objects. Such materials are employed to reduce the opportunities for contamination of the surfaces of objects with dust, and to prevent contact and abrasion between two adjacent objects while in storage. When objects are packed closely and the covering materials are pressed onto the surface of the plasticized PVC, migration of plasticizer can take place from the object to the absorbent material .

Objective of the research project

The main objective of this study was to establish strategies which would extend the useful lifetime of plasticized poly (vinyl chloride) (PVC) for a longer period than was currently usual in the museum environment. In order to achieve the main objective, three minor goals were set. These were to:

1. Define the major mechanisms by which plasticized PVC deteriorates in the collections of museums. In this thesis, the term ‘deterioration’ is used to describe any irreversible change in optical, physical or chemical properties of the material.

2. Develop a non-destructive analytical technique to quantify the extent to which the most damaging degradation mechanism takes place.

3. Devise and evaluate storage strategies which would inhibit degradation of plasticized PVC, while meeting the constraints of the museum environment. Successful strategies were to be inexpensive to implement, of low practical complexity and were to allow public accessibility to plastics objects.

4. Deterioration of plasticized PVC in the museum environment

Examination of plasticized PVC in the care of the National Museum of Denmark

Objects in the care of the National Museum of Denmark were examined to establish the major types of deterioration experienced by plasticized PVC found in a museum with mixed collections. The six objects described here represent both the range of object types and deterioration observed in the Museum's collections.

The surfaces of all objects were analysed non-destructively using Attenuated Total Reflection Fourier Transform Infrared (ATR-FTIR) spectroscopy. Spectra were collected over 30 scans at a resolution of 4 cm^{-1} between 4000cm^{-1} and 600cm^{-1} using an ASI DurasamplIR single reflection accessory fitted with a diamond crystal in a Perkin-Elmer Spectrum 1000 spectrometer. Further details of this technique are given in Chapter 5,'Experimental methods'.

A Jeol SM LV-5310 scanning electron microscope (LV-SEM) was used to examine the surface morphology of selected objects. Samples (3x3mm) were adhered to aluminium stubs and examined at magnifications of x150 and higher. Since the microscope operated at low vacuum, no further preparation of samples, such as coating which is usually necessary with SEM examinations, was necessary. A beam current of 10kV was found to produce a detailed image without damaging the sample.

In addition to examination of the surface, cross-sections of selected samples were also examined by LV-SEM. Since most plasticizers are readily absorbed by waxes, polyester and epoxy embedding resins, no mounting was made. Instead, a thin strip (10 x 2 x 1mm) was cut, using a microtome blade to straighten the edge to be examined, and trapped between two parallel glass microscope slides, so that it overhung by 3mm. The microscope slides were mounted vertically in the LV-SEM chamber, so that the sample could be examined end-on, parallel to the detector.

Exhibition poster

The poster was produced to advertise an exhibition 'The Plastics Age; From Modernity to Post-Modernity' hosted by the Victoria & Albert Museum and a department store, Liberty, in London in 1990. It was constructed from a sheet of transparent, clear plastic material , 500 x 750x 0.25mm, sufficiently flexible to be rolled to fit into a card storage tube,150mm in diameter, and illustrated with images of plastic furniture, kitchenware and other pieces, which had been applied from the back side.

Environment history

The poster was collected at the time of the exhibition and was displayed on an east-facing wall in an uncontrolled environment for 10 years (Figure 4.1). Adhesive tape had been used to mount the poster.

Deterioration

An area 100mm wide and the length of the poster had yellowed along the real left -hand edge (Figure 4.2). No difference was detected in the flexibility or hardness between the discoloured and transparent areas.

Figure 4.1 PVC poster advertising 'The Plastics Age; from Modernity to Post-Modernity'

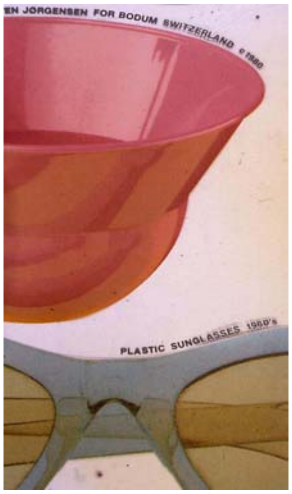


Figure 4.2 Yellowed section of poster

Analysis

ATR-FTIR spectroscopy was used to identify the construction material of the poster. The spectrum was a good match with that of PVC plasticized with DEHP.

Microscope cover

It was constructed from sheets of flexible PVC and had been transparent when new. Machine-stitched seams at the sides and lower edges were used to produce a ridge-tent construction, 450mm wide and 480mm high.

Environment history

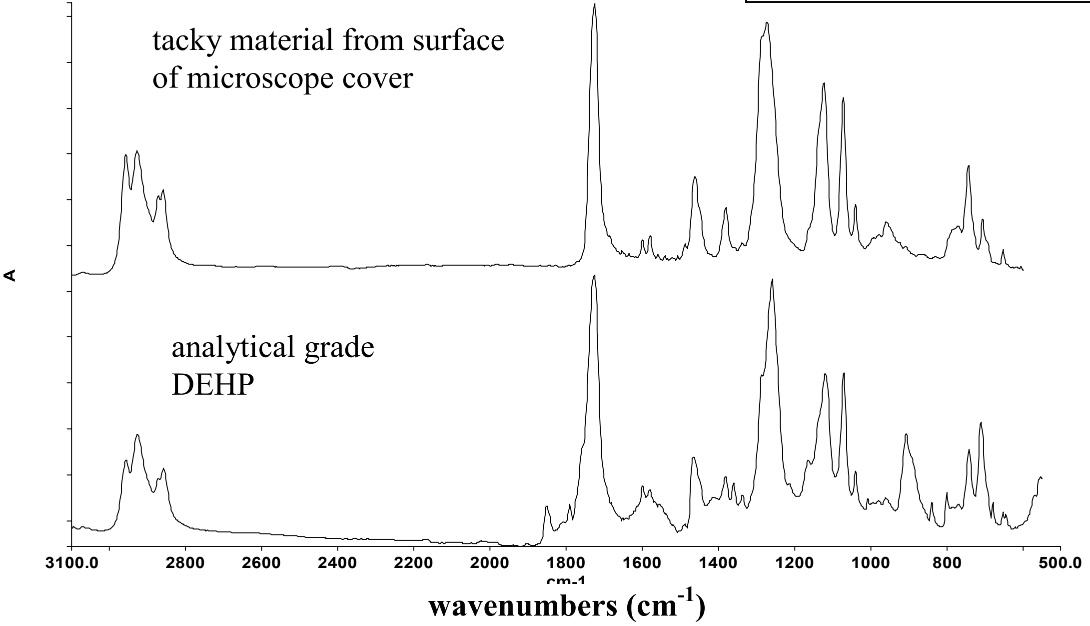
The optical microscope cover had been in use for 15 years in a laboratory. Temperature and RH were not controlled during that period.

Deterioration

The plastic used to construct the microscope cover was no longer transparent, but had developed a cloudy appearance (Figure 4.3). Particles of dust and fibres adhered to the outer surface, which was tacky when touched. Yellow patches were randomly distributed over the surface, particularly close to the lower edges.

Figure 4.3 (left) Microscope cover had developed a cloudy appearance and was tacky to the touch

Figure 4.4 (below) ATR-FTIR absorbance spectrum of tacky material from surface of the microscope cover was a good match for DEHP



LV-SEM examination of the surface showed a homogeneous, featureless surface. The outer surface of the microscope cover and cross-section were also mapped for distribution of elemental carbon, oxygen and chlorine using the LV-SEM. Chlorine was associated only with PVC and not with plasticizer, while oxygen was used as an indicator for DEHP (Figure 4.5).

Both elemental chlorine and oxygen were present on the outer surface of the microscope cover. Examination of the cross-section showed higher concentrations of oxygen at the surface compared with the bulk suggesting that a layer enriched with DEHP achieving a maximum thickness of 0.1mm was present at the surface. Mapping showed there to be a lower concentration of PVC indicated by chlorine, in this layer than in the bulk.

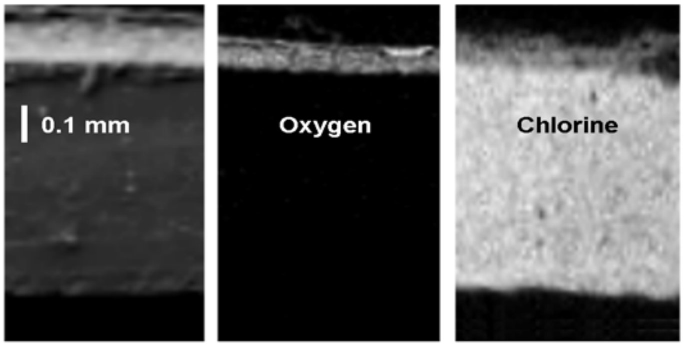


Figure 4.5
Scannnng electron micrographs of microscope cover. Secondary electron scan (far left) and elemental maps of oxygen and chlorine in cross-section of microscope cover. Brighter regions contain highest concentrations of the named element.

Insulation sleeve from aircraft

The aircraft was a Republic F-84G Thunderjet believed to date from the 1950s and, since it was manufactured in the USA following World War II, its construction used the newest materials and technology available at that time. It was owned by the Royal Arsenal Museum, Copenhagen, Denmark and registered as aircraft number 9978 FS-978. For convenient storage, it had been separated into three sections, namely the body, one wing and tail. Insulation on a connecting cable in the body section was the component of interest. It acted as an insulating sleeve, enclosing and holding ten cables in position and was attached to a metal connector which was highly corroded (Figure 4.6). The cables had been positioned close to the engine when the aircraft was used.

Figure 4.6 Deteriorated PVC insulation on a connecting cable (upper left of figure) in section of Republic F-84G Thunderjet. Insulation cable was 6cm in diameter.

Environment history

The extent of the aircraft's active life was unknown, but it had been stored in a large hanger at Tirstrup Airfield, Denmark for twelve months at the time of examination. The hanger was constructed from a metal shell and was not insulated from outside conditions.

Deterioration

The insulating sleeve had a dark brown outer surface which was considerably darker than the interior surface in contact with the cables. It was also extremely brittle, and could be broken into fragments using only finger pressure. Pieces were missing from the sleeve, revealing the underlying cables. Shrinkage of the sleeve was also evident on examination.

Analysis

ATR-FTIR spectroscopy of the insulation sleeve suggested that it was PVC, a polymer commercially developed in 1928 to replace natural rubber for electrical insulation. The presence of a strong peak at 1723cm-1 suggested the presence of a carbonyl-containing material, most likely to be an ester. In such a PVC formulation, plasticizers are the most likey source of esters, suggesting their presence in this case(see Figure 4.7).

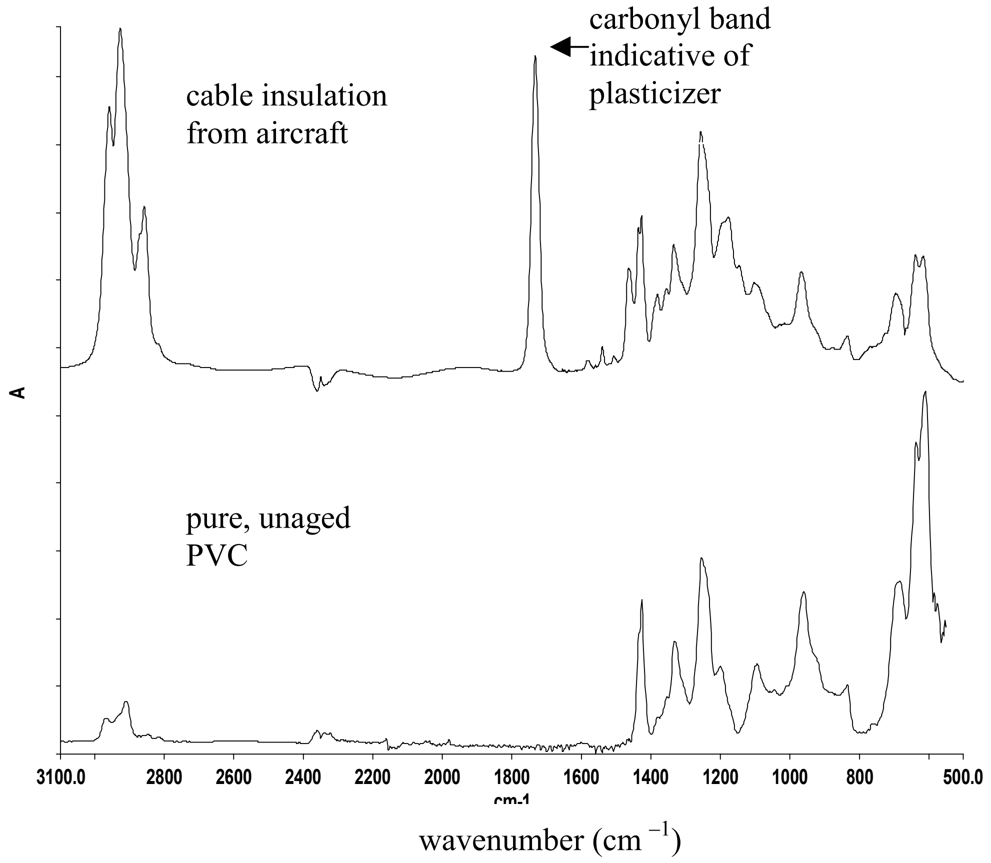


Figure 4.7 ATR-FTIR absorbance spectrum of cable insulation was a good match for plasticized PVC

LV-SEM was used to examine the condition of the surface of the sleeve. At x500 magnification, the surface appeared to be fragmented and pitted.

Life support tubes from Apollo space suit

In March 2000, a two-year conservation project was initiated by the National Air and Space Museum (NASM) in Washington DC, USA and involving industrial scientists and conservation professionals in many institutions worldwide. Its purpose was to establish the various types of deterioration exhibited by spacesuits from the Apollo Space program, and to use that information to develop a conservation policy to preserve them for future study (Young, 2000). The Apollo suits were the first and, from a technical and historical viewpoint, the most important suits in the NASM collections. All the suits from this time period were either custom made for each astronaut, or were developed as prototypes. They contained 22 different materials. The author was invited to examine the various PVC components of the Apollo suits, one of which is described here.

PVC tubing (15mm outside diameter) encased within nylon textile, was used for life support hoses which carried water and oxygen from portable oxygen life support systems to the astronauts during lunar activity. The name Tygon B43 was stamped onto the outer surface of the tubes. This grade of PVC tubing was manufactured for food and beverage use in the 1960s.

Environment history

Lunar activity meant that suits were exposed to temperatures between –150ºC and 120ºC, cosmic radiation and high speed meteroid particles in a gravity one sixth that on Earth. Spacesuits at the National Air and Space Museum have been exposed to a variety of environments. Many of the suits remained in their original packing cases while the specially designed Garber Facility for conservation of space equipment was prepared. In 1975 the spacesuits were relocated to the new facilities, where they were hung in tall, cedar-lined cases (Baker, 1993).

In the 1980s, the majority of suits in the collection were placed in cool storage at 45% RH and 5ºC. At the time, such environments were regarded as suitable for mixed media and organic objects, in the absence of established guidelines for objects containing modern polymers. Low temperatures and RH were thought to reduce the rate of chemical deterioration reactions. Metal shelves were used to support the suits inside closed cabinets.

Until 1978, there was an active program of loaning space suits to other institutions; it is likely that during transport and installation, they were exposed to large variations in temperature and RH.

Deterioration

Visual examination of the life support tubing showed two, apparently progressive stages of deterioration on internal and external surfaces.

- Liquid stage. Droplets or thin films of liquid were visible on the surface of the tubing and the PVC was tacky to touch. Pools of liquid were sometimes present, causing staining of adjacent suit materials. Shrinkage, embrittlement and severe discolouration of the PVC itself were associated with this stage .

- Crystalline stage. Dense, white crystalline material adhered to the discoloured, tacky PVC (Figures 4.8 and 4.9). Dust and packing materials had adhered to the deteriorated surface.

In the 1980s, scientists at the National Air and Space Museum examined the PVC tubing and documented that it had started to weep plasticizer (Baker, 1993). Evidently, the deterioration process had continued since that time.

Figure 4.8 Yellowed life support tubing from Apollo space suit showing crystalline phthalic acid on inner and outer surfaces. The tube is 15mm in diameter

Figure 4.9 Crystals on inside surface of life support tube

Analysis

ATR-FTIR spectroscopy indicated that droplets and thin films of liquid on the outer surface of the tubing were DEHP while the white crystalline material was identified as phthalic acid (Figure 4.10).

As esters, phthalate plasticizers are susceptible to hydrolysis when exposed to strongly acidic or alkaline conditions. Phthalic acid or anhydride and alcohol are the products of such reactions. In addition, oxygen attack on the two identical tertiary carbons in the alkyl groups of the plasticizer molecule also results in the formation of phthalic acid. Such oxidative reactions are expected to occur above 200ºC, environments not experienced by Apollo spacesuits, but acidic conditions lower the necessary temperature (Wilson, 1995). PVC components from spacesuits were likely to be exposed to highly acidic conditions by the dehydrochlorination reaction of degrading PVC polymer.

LV-SEM was used to locate DEHP and phthalic acid on interior and exterior surfaces, by mapping for elemental oxygen, present in both compounds. Cross-sections of the tubing were also examined. Images at x500 magnification suggested that crystals of phthalic acid were only present at surfaces of the tubing where oxygen was available, and not in the walls. Discrete areas containing oxygen were identified on surfaces of the tubing, while lower concentrations attributed to DEHP, were present in the walls of the PVC tubing (Figure 4.11).

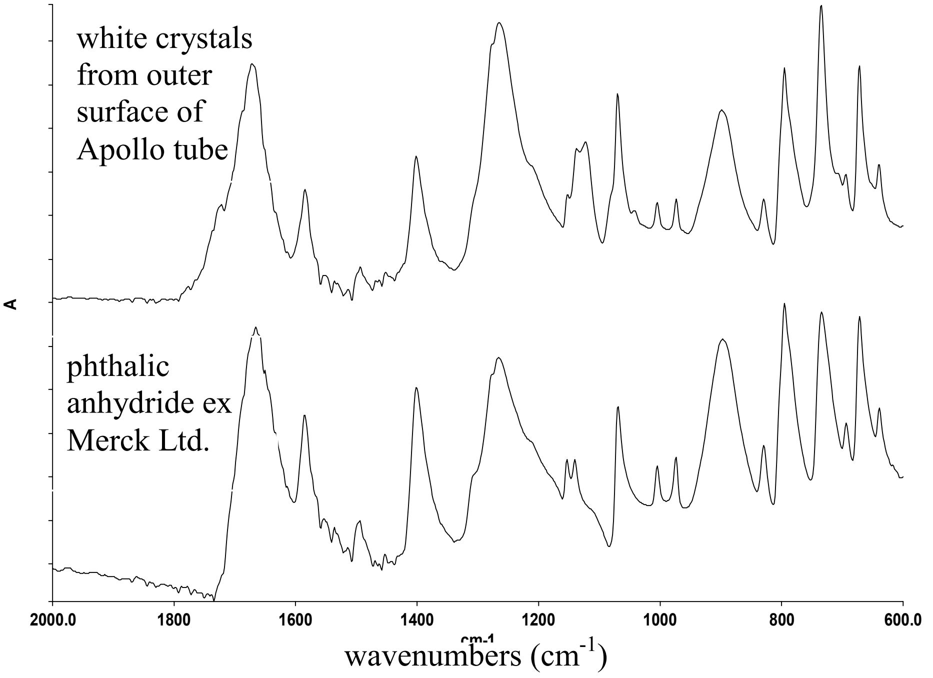


Figure 4.10 White crystalline material on the outer surfaces of Apollo tube was identified as phthalic acid by ATR-FTIR spectroscopy

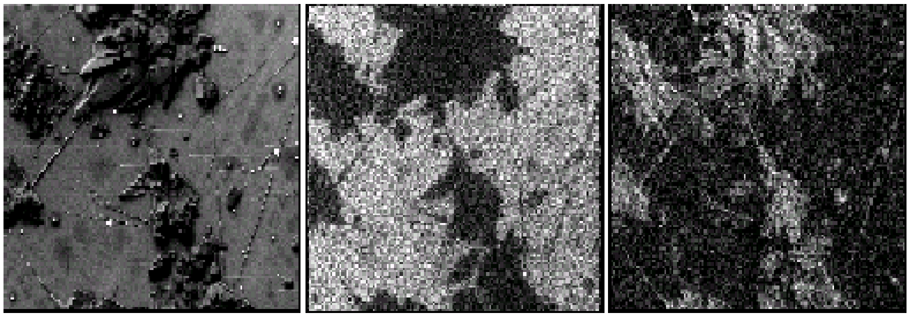


Figure 4.11 LV-SEM scan (far left) shows crystalline, leaf-shaped, degradation products on inside surface of life support tube from Apollo suit. Elemental maps for chlorine (centre) and oxygen (far right) show the crystals contain higher concentrations of oxygen (brighter) than the tube, indicating the presence of a degradation product of DEHP. Sample was 1mm x 1mm.

Photograph pocket

Transparent, plasticized PVC pockets were used to protect photographic material from abrasion during storage with other material and from finger grease during study in the

National Museum of Denmark until the mid-1990s. Such pockets are now systematically being replaced by polyester, due to the deterioration of the PVC pockets and the risk of damage to the enclosed photographic material from degradation products.

Environment history

The photographic collection was stored in closed metal filing cabinets in an uncontrolled environment. Some, but not all of the photograph pockets were interleaved with card.

Deterioration

A colour positive from the Ethnographic Collection (EN94) mounted in an acid-free card frame, depicting a painting by Albert Eckhout, exhibited typical damage due to storage in a photograph pocket for about 15 years. The pocket was constructed from a sheet of plasticized PVC heat welded on three sides to a sheet of polypropylene. The pocket had deteriorated only on the PVC side, in the rectangular area corresponding to the window in the card frame (125 x 110mm), directly above the positive image (Figure 4.11).

Severe cockling and distortion of the pocket were observed in that area, but no discolouration. The image present on the positive was largely obscured by a layer of white crystals, unevenly distributed to form a pattern across the surface (Figure 4.12). The arrangement of crystals correlated well with the points at which the cockled PVC sheet made contact with the surface of the colour positive.

Figure 4.11 Cockled and distorted PVC photograph pocket

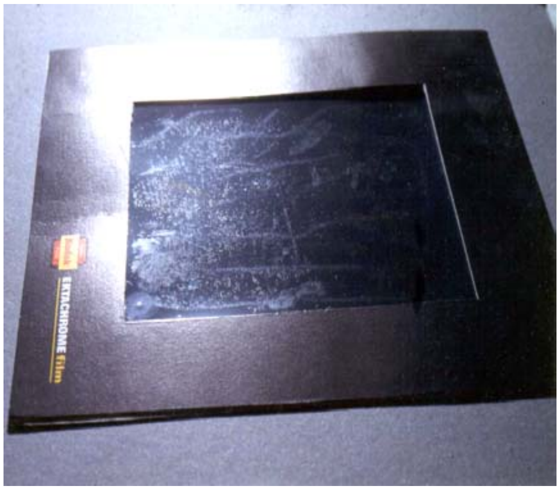


Figure 4.12 Crystals of phthalic acid deposited on photographic positive from PVC photograph pocket

Analysis

ATR-FTIR spectroscopy indicated that the major components present in the degraded section of the photograph pocket were PVC and DEHP. A sample of the crystals was taken from the surface of the colour positive and analysed using ATR-FTIR. The spectrum was an excellent match with that of phthalic acid.

Since the object itself contained neither PVC nor DEHP, it is likely that DEHP diffused out of the photograph pocket and evaporated into the small airspace (approximately 13cm^3) between itself and the positive. When the airspace became saturated with DEHP vapour, it condensed onto the surface of the positive forming a thin film. With time, and favourable conditions, the condensed film degraded to form crystalline phthalic acid, as described for the Apollo life support tube.

In addition, it is possible that when the PVC sheet began to cockle due to the loss of DEHP, some areas of its surface touched that of the colour positive. DEHP on the cockled surface was adsorbed onto the surface of the image in the areas where they touched. It later degraded to form phthalic acid forming a pattern corresponding to the areas of contact.

Teenage doll

The hollow doll was manufactured in the 1970s and had dark, nylon hair and flexible, opaque, flesh-coloured skin. She wore a sleeveless, knee-length cotton dress closed at the back using three metal fasteners. Arm and legs were jointed at the shoulder and hips. Joy Boutrup, Head of the Textile Conservation Section, The National Museum of Denmark drew my attention to the poor condition of this doll.

Environment history

After use, the doll had been stored in a house cellar for 20 years in a cardboard box. The temperature and RH in the cellar were not controlled. At the time of storage, the doll was in good condition.

Deterioration

On removal from storage, there was a dramatic change in the doll’s appearance. A dense, white, hard material obscured 90% of the area of the skin on both legs and on the body under the dress, while neck, face, arms and hands had only discrete patches of the white material (Figures 4.13 and 4.14). It was not possible to remove the material by brush, due to its good adhesion to the doll’s skin. It was noted that the skin of the legs had become brittle and could not be flexed under finger pressure.

Analysis

ATR-FTIR spectroscopy of the back of the doll's right hand, the only area sufficiently clear of degradation products and convenient to position in the FTIR spectrometer to sample only the plastic, produced a spectrum attributed to PVC plasticized with DEHP (Figure 4.15). A spectrum of the white degradation product was a good match to stearic acid. A few peaks attributed to the presence of DEHP were also present in the spectrum.

Figure 4.13 Teenage doll exhibiting white crystalline material on legs, body and arms. The doll was 40cm high

Figure 4.14 Doll's legs showing a high concentration of stearic acid crystals on surface

Three possibilities for the origin of stearic acid were considered. Natural and synthetic esters of fatty acids were among the earliest plasticizers for PVC (Sears and Darby, 1983). However, their tendency to oxidize readily to form the corresponding acid led to their exclusion from commercial PVC formulations prior to 1970, the approximate date of manufacture of the doll. It seemed unlikely therefore that this was the origin of the stearic acid.

Calcium carbonate powders used as fillers in PVC may be treated with substances which make the particle surface hydrophobic, thereby facilitating certain processing and performance performances. Moisture absorption by surface-treated particles is reduced which improves flow of the powder and reduces agglomeration. The amount of plasticizer required to coat the surface of treated filler particles may be reduced by up to 35% (Titow, 1984). Stearic acid and some stearates are the oldest and still the most widely used reagents. Such materials may either be mechanically deposited on the particle surface or reacted with it at elevated temperatures and pressures. In the former case, a change in the surrounding environment, perhaps the increased relative humidity in the house cellar, may have caused stearic acid to separate from the filler and migrate to the surface.

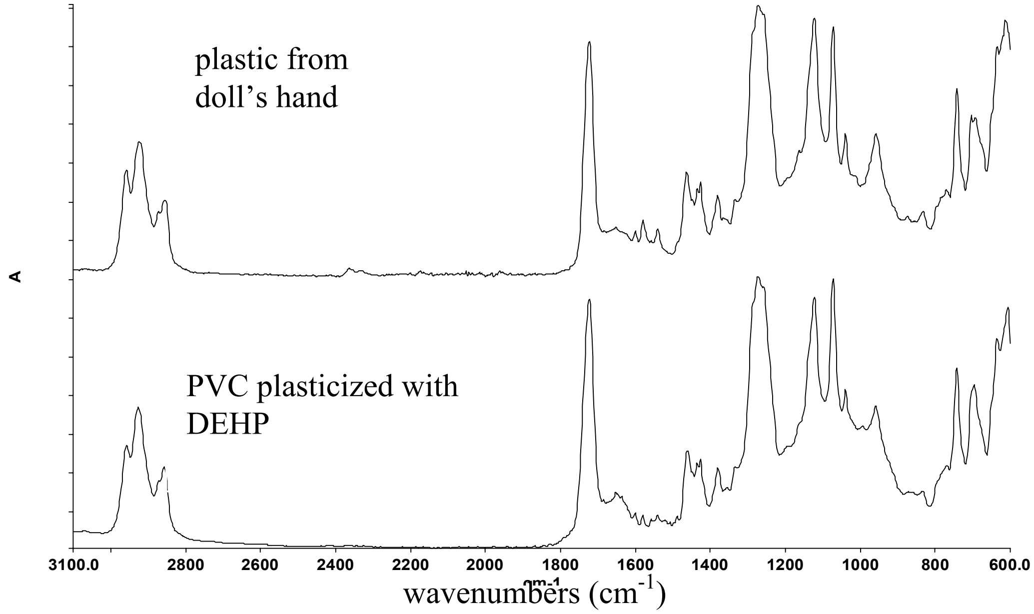


Figure 4.15 FTIR spectrum of plastic on back of doll's real right hand was a good match for PVC plasticized with DEHP

Most plasticized PVC formulations contain a small amount (between 1 and 3% by weight) of a lubricant to prevent excessive adhesion to the mould during production. Such adhesion would slow production and result in a product with a faulty surface. The most common lubricant is stearic acid (Sears and Darby, 1982). Stearic acid is almost completely incompatible with PVC, due to its molecular structure; it can readily form hydrogen bonds at one end and is extremely non-polar at the other, while PVC is polar due to the carbon-chlorine dipole. It is, however, a better solvent for DEHP. It was concluded that during storage, stearic acid separated from the PVC skin of the doll and migrated to the surface. It was not possible to establish whether the lubricant first dissolved and carried the DEHP during its migration to the surface or dissolved DEHP already at the skin surface during this process.

Conclusions from examination of plasticized PVC in the museum environment

Examination and analysis of deteriorated objects suggested that although discolouration due to dehydrochlorination of the PVC polymer was aesthetically damaging, surface tackiness due to the presence of plasticizer at the surface was of greater importance from a conservation perspective.

- Tacky surfaces reduced storage and handling possibilities. Packaging materials adhered to such surfaces making storage and transport of deteriorated objects difficult. Particulates and fibres, suspended in surrounding air, adhered to tacky surfaces, obscuring surfaces and disfiguring objects.

- Phthalic acid crystals at surfaces of plasticized PVC, formed either by oxygen attack on alkyl groups or hydrolysis of the ester groups of DEHP , disfigured surfaces and were readily offset onto any objects in contact with the degraded PVC, potentially accelerating the rate of deterioration of those objects.

- Finally, but of extreme importance, there was concern that handling and contact with objects made tacky due to migration of plasticizers to objects' surfaces may pose a risk to health for staff and students. DEHP has been identified in aquatic environments, in air, in foodstuffs and in the human body. Many symptoms and illnesses have been attributed to DEHP including its ability to behave as an oestrogen mimic, but it is difficult to obtain unbiased, scientifically-based data.

  The Scientific Committee on Toxicity, Ecotoxicity and Environment has expressed its concern about the risks resulting from the exposure of small children to DEHP and DINP used in toys and childcare articles, due to the potential adverse effects on liver, kidney and testicles. The European Union Commission adopted a Decision under the emergency procedure of Directive 92/59/EC in December 1999 in order to ban the use of phthalates in certain toys and childcare articles intended to be put in the mouth.

  The European Union Commission produced a Green Paper entitled 'Environmental issues of PVC' in May 2000, which reviewed the data and promoted discussion about future legislation concerning , in particular, the use of phthalate plasticizers and lead-containing stabilizers in PVC (European Union Commission, 2000). Without waiting for full risk assessments to be completed, the Danish government has adopted an action plan to reduce the use of phthalate by 50% by the year 2010 (Bostrup, 2000).

  The concern about health risks from such objects in museums arises from the fact that museums are likely to keep old PVC formulations for a longer period than their commercial useful lifetime. In this way, museum staff are likely to be in contact with PVC in an advanced state of degradation.

For these reasons it was decided to investigate the factors associated with loss of plasticizer, and the possibilities for inhibiting its migration. Since the most common plasticizer identified in museum objects was DEHP, the investigation focused on this material.

5. Experimental methods

Overview of experimental design

Examination and analysis of deteriorated museum objects containing plasticized PVC suggested that migration, loss and chemical breakdown of plasticizer were the major mechanisms of deterioration observed when museum objects were stored. The purpose of the experimental work was to develop techniques for quantifying the amount of plasticizer lost by evaporation and that present on the surface during deterioration. Those techniques were used to compare the effect of various environments, commonly used in museum storage areas, on the rate and extent of deterioration of plasticized PVC formulations.

Since it was both unethical to experiment on registered museum objects and difficult to obtain sufficient homogeneous material with a known environmental history, model samples were prepared to represent the full range of PVC formulations present in museum collections. The plasticizer most frequently identified in museum objects was DEHP, so the investigation focused on this material.

Model sheets were exposed to various environments, all of which are frequently used to store and display plastics and other materials in museums. Due to lack of time and the possibility of comparing the results obtained with those of other researchers, accelerated thermal ageing was used instead of natural ageing. In addition, two naturally aged ‘objects’, also plasticized with DEHP and exhibiting deterioration, were included in the experimental work to examine the effect of the environments on non-ideal materials.

Non-destructive examination techniques were used to identify and quantify changes in visual, chemical and structural properties of the samples during thermal ageing (Table 5.1).

Preparation of model PVC formulations

To prepare small, laboratory-scale samples, two techniques were considered. The first of these was to cast thin sheets from a solution of PVC in tetrahydrofuran using a doctor blade. Tetrahydrofuran is a highly toxic solvent, and was likely to produce sheets from which residues of solvent could not be completely removed without the application of heat. Such treatment was likely to promote thermal degradation of the PVC itself. In addition, the use of tetrahydrofuran tends to promote aggregation of PVC molecules, resulting in a sheet with inhomogeneous composition (Lyngaae-Jørgensen, 1976).

Table 5.1 Examination techniques applied to model sheets and 'objects'

technique	**frequency of measurement during thermal ageing**	**depth of analysis**	**information**
visual examination/ photography	every 7 days	whole sample	change in colour, surface appearance and tackiness on ageing
weight loss	every 7 days	whole sample	quantitative loss of volatiles eg plasticizer
Attenuated Total Reflection-Fourier transform infrared (ATR-FTIR) spectroscopy	every 7 days	approximately 2µm, depending on wavelength	functional groups and quantitative measurement of plasticizer at surface
Low-vacuum scanning electron microscopy (LV-SEM)	as required	2-3µm	morphology, physical microstructure and elemental composition of surface and cross-sections
densitometry / area of discolouration	before and after ageing period	whole sample (approximately 0.5mm)	optical density of samples, proportion of sample which appears darker due to deterioration
headspace analysis-gas chromatography and Universal indicator paper	as required	not applicable	qualitative identification of organic components and HCl in volatiles produced during thermal ageing

The second technique considered, and subsequently used, was to press sheets from PVC plastisols using a heated hydraulic press. This approach was considered a more readily-controlled technique and one which produced sheets without solvent residues.

Plastisols comprise a liquid dispersion of ingredients, which are mixed and shaped at ambient temperatures; only heating is required to initiate the transition from mixture to homogeneous compound. Since it was not possible to obtain a series of ready-made sheets of similar thickness, varying only in their plasticizer content from a commercial source, plastisols were obtained, their plasticizer concentrations adjusted to the required concentration and model sheets prepared in the laboratory.

Samples of two plastisols, based on DEHP and commercially prepared by polymer companies Hydro Polymers in Norway and Solvay Chemicals based in Belgium were used to prepare model sheets. The basic formulation of the Hydro plastisol is shown in Table 5.2 and is typical of that used to produce heavy duty, thick-walled tubing and shoe soles.

The plastisol supplied by Solvay was a lower viscosity material supplied with 20phr, equivalent to 16.7% DEHP by weight, and barium/zinc laurate as a thermal stabilizer according to the accompanying technical information. It was a formulation typical of that used for products with low sheet thickness including hollow toys and vinyl flooring.

Pigments were omitted from the model formulations since they were likely to confuse measurement of discolouration by the PVC component.

Table 5.2 Formulation of Hydro plastisol

component	**function**	**amount (parts per hundred of resin)**
medium molecular weight PVC, weight average 200,000	polymer	100
DEHP	plasticizer	50 (33.3% based on PVC plus DEHP)
barium/zinc laurate	thermal stabilizer	
epoxidized ester of mixed fatty acids	co-thermal stabilizer	

To produce model sheets containing the range of plasticizer concentrations found in museum collections, both plastisols were diluted using DEHP. An electric paddle mixer was used to incorporate additional plasticizer thoroughly, resulting in calculated DEHP concentrations of 16.7%, 23.1%, 28.6%, 33.3%, 37.5%, 44.4% and 50%. These formulations represented the full range of PVC formulations found in museums. It was only possible to prepare plastisols containing 16.7%, 23.1% and 28.6% from the Solvay feedstock; all others were available from both Solvay and Hydro plastisols.

Preparation of model PVC sheets

At ambient temperatures, plastisols essentially contain PVC particles dispersed in liquid plasticizer. When the plastisol is heated, plasticizer is first adsorbed onto the surface of the PVC polymer particles; this is often referred to as the gelation stage. Temperatures higher than 160º C are necessary for the particles to fully merge and form a physically homogeneous plasticized PVC material with maximum mechanical properties, a state known as fusion. Preparation of sheets may be regarded as a phase inversion process; intially solid PVC is dispersed in liquid plasticizer; on completion of fusion, plasticizer is dispersed in the PVC matrix.

Commercial moulding of PVC is usually conducted at temperatures between 180ºC and 220ºC. However, since the volumes of plasticized PVC to be prepared were very small, it was considered important that temperatures were kept as low as possible and maintained for the minimum period necessary to achieve fusion. In this way, discolouration of the produced sheet, due to thermal degradation of the PVC, was avoided.

Laboratory trials showed that 180ºC for 90 seconds was the lowest temperature and shortest period necessary to achieve complete fusion without yellowing. A metal frame (90 x 90 x 0.8mm) was placed on a thin sheet of aluminium foil which, in turn, was placed on the pre-heated base plate of a hydraulic press. Approximately 9mL of plastisol, a small excess, were poured into the frame from a height of 5cm to avoid incorporation of air into the liquid.

The plastisol was allowed to spread and fill the frame for 3 minutes, also allowing any incorporated air to migrate to the surface. A second sheet of aluminium foil was placed over the filled frame and the press was closed. After 90 seconds, the press was opened and the PVC sheet allowed to cool at room temperature, before removing from the frame. Any excess liquid plastisol was pressed out of the frame, onto the foil, fused during heating and was readily removed in solid form on cooling.

Model sheets were interleaved between pieces of aluminium foil, and stored under ambient conditions (20 ± 3º C) for 14 days between preparation and ageing or testing. Standard mechanical testing procedures specify that plasticized PVC should be conditioned for at least 7 days to avoid ‘false’ results (ASTM D 3291).

The outer 5mm edge was cut from all model sheets before taking samples to use in ageing experiments. This practice avoided the use of areas which may have been thicker than the body of the sheet. Rectangular-shaped samples weighing 1g (approximately 50mm x 30mm) were cut from the sheets for inclusion in accelerated ageing experiments, and weighed on an electronic analytical balance to 4 decimal places.

Characterization of model sheets

Model sheets were characterized by physical thickness and chemical composition of extracted material

Thickness measurements
Thickness was measured using a micrometer screw gauge; an average was calculated of six measurements from two sheets at each plasticizer concentration (Table 5.3). There was a small variation in the order of hundredths of a millimetre.

Table5.3 Thickness of model sheets

model sheet description	**mean thickness at 25°C (± 0.01) mm**
Hydro 33.3%	0.56
Hydro 37.5%	0.57
Hydro 44.4%	0.55
Hydro 50.0%	0.53
Solvay 16.7%	0.51
Solvay 23.1%	0.53
Solvay 28.7%	0.56
Solvay 33.3%	0.50
Solvay 37.5%	0.52
Solvay 44.4%	0.50
Solvay 50.0%	0.49

Chemical composition of extract
Soxhlet extraction in distilled diisopropyl ether (boiling point 60ºC) was carried out on examples of the model sheets prepared from the plastisols supplied by Hydro and Solvay to establish the concentration of DEHP after pressing and conditioning. Finely-divided samples of films (2g) were extracted in diisopropyl ether (20mL) for 6 hours before drying the extract to constant weight (± 0.0002g). Extraction was repeated in triplicate for each sample and the mean plasticizer content calculated (Table 5.4).

Table 5.4 Mean plasticizer content measured in Hydro and Solvay plastisols

Supplier of plastisol	**DEHP in supplied plastisol, calculated (% by weight)**	**mean extracted material from model sheet (% by weight)**
Hydro	33.3	37.5
Solvay	16.7	37.4

Hydro plastisol was known to contain 4% by weight thermal stabilizers; since they are stable up to temperatures of 200°C, it was assumed that they would not have evaporated during preparation of the model sheets, and would be extracted with DEHP in diisopropyl ether. Taking that into consideration, the calculated concentration of DEHP in the plastisol was very similar to that measured in the sheet. The process used to prepare model sheets had caused minimal loss of plasticizer.

In contrast, Soxhlet extraction of model sheets produced from Solvay plastisol gave unexpectedly high percentages of material. Although the percentage of thermal stabilizers had not been disclosed by the supplier, it was not expected to exceed 4% as present in the Hydro material. This left more than 16% of extracted material unaccounted for.

Thin-layer chromatography (TLC) was used to separate and, subsequently, identify the extracted components of Hydro and Solvay model sheets. Extracts and reference samples of plasticizers known to be used in plasticized PVC formulations, were diluted in ethyl acetate (to form solutions 10% by volume) and spotted onto the surface of a Whatman silica gel (250μm layer) thin layer chromatography plate, 1cm from the lower edge. The solvent medium used in the chromatography tank was 9:1 iso-octane:ethyl acetate by volume, a blend of non-polar and polar solvents respectively (Stahl, 1969). The dried plate was placed in the tank and the solvent blend allowed to carry the samples half the height of the plate before it was dried and developed using iodine vapour. The positions of all spots were marked and the distance each had migrated from its starting position was measured.

Examination of TLC plates indicated that extracts from both Hydro and Solvay films contained DEHP. In addition, Solvay films contained one component not present in Hydro films. FTIR spectroscopy of the Solvay extract indicated that the additional component contained the same chemical groups as DEHP, but was an aliphatic rather than an aromatic compound.

The additional component in the Solvay extract found by TLC was identified as Eastman TXIB (2,2,4-trimethyl-1,3-pentanediol diisobutyrate) by comparing the unknown with a reference FTIR spectrum. Eastman TXIB, formerly known as Kodaflex TXIB, is the lowest viscosity plasticizer used commercially in PVC (Figure 5.1). Eastman TXIB may replace a proportion of the general-purpose plasticizer with the purpose of lowering the viscosity of plastisols and, therefore, the energy required to process them (Eastman Chemicals, 2001). In addition, TXIB imparts a less tacky and more stain-resistant surface to products compared with those formulated only with DEHP. Its main applications are in the manufacture of hollow toys and sheet vinyl flooring; it has been included in selected formulations since the mid 1960s (van der Sluijs, 2001). Eastman TXIB has approximately the same efficiency or amount required to achieve a given hardness in the final product as DEHP, so is generally used to replace some portion of it on a 1:1 basis.

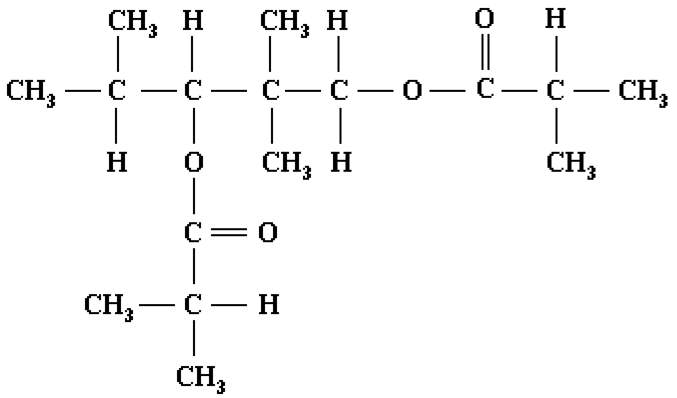


Figure 5.1 Chemical structure of Eastman TXIB

Solvay confirmed that this was the case in the present plastisol, and that it contained 16.7% DEHP and the same percentage of TXIB (Patrick, 2001). This fitted exactly with the percentage material extracted from the model sheets and confirmed that the process had caused minimal loss of plasticizer. Since DEHP alone was used to dilute the Solvay plastisol and produce the series of model sheets, the percentage of TXIB decreased as that of DEHP increased. The percentage plasticizer content of Hydro and Solvay model sheets, based on the total polymer and plasticizer content is shown in Table 5.5.

Table 5.5 Percentage plasticizer composition in Hydro (DEHP only) and Solvay (DEHP and TXIB) model sheets

composition of plasticizer in Hydro model sheets	**composition of plasticizer blend in Solvay model sheets**		
% DEHP by weight	**%DEHP by weight**	**%TXIB by weight**	**% total plasticizer by weight (DEHP +TXIB)**
	16.7	16.7	33.4
	23.1	15.4	38.5
	28.6	14.3	42.9
33.3	33.3	13.3	46.6
37.5	37.5	12.5	50.0
44.4	44.4	11.1	55.5
50.0	50.0	10.0	60.0

Preparation and characterization of ‘objects’

Two naturally aged PVC materials, were included in the experimental work to evaluate the effect of various storage environments on the rate of further degradation of objects already exhibiting deterioration. A microscope cover had been in use for 15 years in the Conservation Research Laboratory, National Museum of Denmark (Figure 4.3). It had developed slight opacity and the outer surface was tacky. Particles of dust and fibres adhered to the outer surface. FTIR spectroscopy suggested that the cover contained DEHP as a plasticizer. Samples (1g) were cut from a side panel, the area which appeared most homogeneous.

A transparent, flexible PVC tube had been used, until approximately 10 years ago, to transport water from the Polymer Laboratory in the Department of Chemical Engineering, Denmark’s Technical University, to an adjacent fume cupboard. Since its ‘retirement’, it had been suspended vertically from a height of 3 metres and was open to air at the lower end. The tube appeared yellow, and was tacky to touch. A white nylon connector had been placed in the lower end of the tube; the space between the connector and tube was filled with approximately 3mL of a yellow liquid. FTIR spectroscopy indicated that the liquid was DEHP which had migrated out of the PVC tubing and collected at the lower end under the influence of gravity. Samples for thermal ageing, 1cm long and 1cm outside diameter, were taken from at least 15cm away from the nylon connector to avoid the area with very high DEHP content. The tube wall thickness was approximately 2mm.

Preparation of storage environments

Model sheets and naturally aged ‘objects’ were exposed to various environments, all of which are frequently used to store and display plastics and other materials in museums (Table 5.6). Accelerated thermal ageing in the absence of light was used because it was thought to represent the natural ageing environment in a store more accurately than accelerated exposure to light.

Commercially, the performance of plasticized PVC sheets, cables and fabric coatings in tests at elevated temperatures is considered to give an indication of likely long-term behaviour in service at ambient temperature. Various temperatures are used depending on the major process to be studied. Standard tests to evaluate production of hydrogen chloride by the PVC component are conducted between 170ºC and 180ºC (ASTM D2115-67,1980 and ISO/R 182,1970). Volatile loss of plasticizers from PVC compounds is evaluated at temperatures of 70ºC (ASTM D1203,1994). Resistance of cable insulation and sheathing to heated electrical conductors is evaluated at 70ºC (Titow, 1984). Resistance to migration of plasticizers is usually determined at 70ºC (DIN 53-405,1981).

Since the major area of interest in this project was the behaviour of the plasticizer component, 70°C was used to accelerate the thermal ageing process; it was also higher than the glass transition temperature, Tg, of all the model formulations used. All storage environments were maintained at 70±1 °C and achieved using a convection oven, with the exception of the freezer (-20±1ºC).

Environments were created in wide-neck Pyrex glass flasks (100mL) fitted with heavy duty melamine resin screw caps lined with polytetrafluoroethylene (PTFE). All materials used were selected for their very low absorption of phthalate plasticizers, high chemical stability and ability to seal the ageing environment from the exterior conditions. Samples of model sheet and naturally aged 'object' were suspended in position in the centre of the flask from fine nylon thread caught between the cap and screw thread. The purpose was to provide equal opportunity for movement of gases and vapours around all surfaces of the sample. All environments were created under ambient conditions before being placed in a cool oven and heated, over 8 hours, to the 70± 1°C ageing temperature. Flasks containing samples for the freezer were placed first in insulated card boxes to facilitate handling, before being put into the cold environment.

Table 5.6 Experimental storage environments used to thermally age model sheets and 'objects'

environment *	**equivalent museum storage**	**function**	**how achieved**
closed	box or other container	exclude dust, buffer climate variations	sheets suspended in closed screw-cap flask
open oven	naturally ventilated storage area or display case	avoid build-up of pollutants	sheets suspended in convection oven
open glass plate	open shelf or cupboard	display	sheets on Pyrex glass plate in convection oven
activated carbon (AC)	activated carbon or activated charcoal cloth	adsorb and remove volatiles	AC placed in base of closed flask
Ageless® oxygen absorber	oxygen-free environment	inhibit oxidation pest control	one Ageless® Z sachet placed in base of each flask, before flushing with N_2
silica gel	low relative humidity (RH)	dry air	silica gel placed in base of closed flask
high relative humidity	high RH	moisten air	water (20mL) in base of closed flask
low density polyethylene (LDPE) bag	self-seal polyethylene bags	exclude dust and facilitate handling	sheet placed in LDPE bag before sealing
freezer (-20°C)	freezer for storage or pest control	inhibit deterioration	sheets suspended in closed flask in domestic chest freezer

** all environments were maintained at 70 ±1°C except for freezer*

Adsorbent materials were used either to modify the properties of the air inside flasks prior to ageing or to remove degradation products formed during the ageing process:

Activated carbon

Activated carbon, available in granules, powder and cloth, adsorbs a wide range of organic vapours as well as odours and water vapour. It has been used to remove nitrogen oxides from a degrading cellulose nitrate puppet, thus inhibiting autocatalytic deterioration (Ward and Shashoua, 1999). Activated carbon of medium particle size (3mm) and vegetable origin, supplied by Prolabo, was used in the ageing tests rather than powder which was likely to adhere to tacky samples. Activated carbon was conditioned at 150ºC for 12 hours and cooled in a desiccator to 20 °C prior to adding to the Pyrex flasks (10g to each).

Ageless® oxygen absorber

Ageless® oxygen absorber is a commercial product originally designed to inhibit the oxidation of foods during transport. It is available as gas-permeable plastic sachets containing finely-divided iron which oxidizes to form iron oxides in the presence of oxygen and water, taking the oxygen from the surrounding environment. The moisture is provided by the presence of potassium chloride in the sachet and is also a by-product of the oxidation reaction (Grattan and Gilberg, 1994**)**. Different grades of Ageless® are available; Ageless® Z is recommended for the preservation of materials with a water content of between 0 and 85%, so was considered suitable for use with plasticized PVC. Ageless® Z has been used as a low-cost, convenient alternative to flushing with nitrogen for long-term oxygen-free storage of natural rubber in the British Museum (Shashoua, 1999). It is claimed that Ageless® oxygen absorber reduces the oxygen concentration of an air-tight container down to 0.01% (100ppm) or less (Mitsubishi Gas Chemical Company, 1987).

To prolong the active lifetime of Ageless® during use, containers were flushed with oxygen-free nitrogen immediately prior to closing. Ageless® Eye is the oxygen indicator supplied with Ageless®; it is in the form of a pressed tablet which changes colour from pale pink (less than 0.1% oxygen) to dark blue (greater than 0.5% oxygen). Previous experience by the author suggested that Ageless® Eye tended to lose its sensitivity to oxygen after approximately six months usage, manifested by unreliable colour changes. Since the ageing period in this project was shorter than the stability period for Ageless® Eye, it was used and added to each container together with one sachet of Ageless® Z. Sachets were renewed weekly after flasks were opened to examine samples of model sheets or ‘objects’.

Silica gel

Silica gel is frequently used in museum showcases and storage containers to adsorb water vapour and achieve a specific RH in the surrounding airspace. The empirically determined quantity of silica gel required to buffer ambient RH is 20 kilograms per cubic metre of display case volume (Cassar, 1995). On the basis of this general rule, 100mL flasks would require 2g of silica gel at 20°C. Since the performance of silica gel at 70°C is not known accurately, an excess (5g) was used. Self-indicating silica gel, supplied by Merck Ltd., was conditioned following the method described previously for activated carbon prior to adding to the Pyrex flasks.

Accelerated thermal ageing procedure

Accelerated thermal ageing of all model sheets and 'objects' was carried out at the same time to minimise the effect on samples of variation in temperature and RH in laboratory and oven. All ageing was continued for a period of 65 days. An initial trial suggested that this period was sufficient to initiate visible deterioration in all model sheets. The maximum period used to evaluate the performance of plasticized PVC in commercial tests is 30 days, 24 hours is more usual. Museum objects are intended to be kept for at least 50 years; the relatively long ageing period was intended to reflect this.

In most cases, model sheets and 'objects' were removed weekly from their ageing environments for visual examination and photography, measurement of discolouration, determination of weight loss, and FTIR spectroscopy. On removing from the oven or freezer, samples were allowed to attain ambient temperature gradually over a period of 3 hours prior to examination. Other examination techniques, LV-SEM and headspace analysis were not carried out weekly, but as needed. All examinations were carried out on duplicate samples aged in two separate flasks to prevent direct transfer of plasticizer between specimens which would complicate results.

Weight loss of model sheets and objects

Weight loss was one of the earliest techniques used to evaluate the performance of plasticized PVC. In the 1950s, permanence of plasticizers was defined as weight loss when plasticized PVC samples were exposed to various conditions during use (Quackenbos, 1954).

Prior to placing in their ageing environments, model sheets and 'objects' were weighed to four decimal place accuracy using an electronic analytical balance. Throughout the thermal ageing process, samples were re-weighed once per week. Samples were removed from their ageing environment, whether it was flask, glass plate or LDPE bag and conditioned to ambient temperature (20-23°C) without patting their surfaces dry. Weight loss was determined immediately prior to examination by FTIR spectroscopy.

Analysis of volatiles produced by model sheets and 'objects' on ageing

Headspace analysis was used to identify the gaseous organic components in the atmosphere inside the flasks produced during thermal ageing. Due to its invasive nature, long measurement time (around 30 minutes) and the problems of condensation forming in gaseous samples between collection from flasks at 70°C and transfer to the gas chromatograph/mass spectrometer for analysis, it was used only to investigate selected samples. A microdrill was used to make a sampling hole in the selected flask's cap, a syringe (1000 microlitre) needle inserted through the PTFE liner and a gas sample withdrawn. The sample was injected into a Varian 3400 III GC/MS. The methodology of GC/MS is detailed by Skoog et al. (1998).

The MS scanned from 29 to 399 m/z in 0.5 seconds (background mass 25) with tuning through autotune. The gas chromatographic column used was a Restek factory-made 30m long, 0.25mm internal diameter, fused silica column, coated with an 0.25µm XTI-5 stationary phase. The column was mounted with a 5m integrated pre-column. Helium was used as carrier gas and the inlet pressure was 14psi. Analytical parameters were:

Injector: Programmable On Column Injector (SPI), 64°C for 1minute, to 315°C at 200°C/minute, 315°C for 53minutes.
Column: 64°C for 1minute, to 190°C at 10°C/minute, to 315°C at 4°C/min, 315°C for 15minutes.
Transfer line: 315°C.

Samples of industrial grade DEHP, Eastman TXIB and analytical grade phthalic acid, phthalic anhydride and 2-ethylhexanol were dissolved in diisopropyl ether (1% solutions) and analysed by GC-MS as comparative reference samples.

It was intended to use headspace analysis to quantify the various gaseous components produced during ageing. In practice, it was not possible due to the condensation of TXIB and DEHP on the cooling syringe needle and glass walls as it was withdrawn after filling. The condensate appeared to contaminate both syringe and the septum at the entrance to the GC column.

The evolution of hydrogen chloride by model sheets and 'objects' during the ageing process was detected using universal indicator paper obtained from Merck Ltd. Moistened indicator paper was placed in the neck of flasks immediately after opening for weekly examination of samples. After 2 minutes, indicator papers were examined for colour change.

FTIR spectroscopy of model sheets and 'objects'

In this study, Attenuated Total Reflection Fourier transform infrared (ATR-FTIR) spectroscopy was used to quantify levels of plasticizer present at surfaces of all samples. The suitability and reproducibility of quantitative ATR-FTIR spectroscopy to study diffusion of small molecules into polymer films, was first demonstrated by Fieldson and Barbari (Fieldson and Barbari, 1993).

Dutta and Graf have also investigated the diffusion of plasticizers from the bulk to the surface of vinyl materials using ATR-FTIR (Dutta and Graf, 1984). In that study, phthalate plasticizer at the surface of PVC films was dissolved by applying ethanol. The rate of diffusion of phthalate from the bulk of the film to replace that removed at the surface was monitored with time using the growth of the absorbance band at 1725cm^{-1}, assigned to the carbonyl peak of the ester group in the plasticizer. This approach was tried by the author, but not adopted for this study because ethanol was still detected in the model sheets after 2 hours, indicating that it had migrated into the film and could act as a solvent for any low molecular weight components present. Instead, samples were examined without previous preparation and without the introduction of organic liquids.

In the study presented, spectra were collected over 30 scans at a resolution of 4cm^{-1} between 4000cm^{-1} and 600cm^{-1} (the lower limit of sensitivity for ATR), using an ASI DurasamplIR single reflection accessory with an angle of incidence of 45° and fitted with a diamond internal reflection element in a Perkin-Elmer Spectrum 1000 FTIR spectrometer. Initial trials showed that 30 scans were the minimum number required to obtain well-resolved spectra for all samples. The high refractive index of diamond compared with that of plasticized PVC (2.4 and 1.5 respectively) allowed absorbance data to be collected from a depth approximately equal to that of the wavelength of the infrared radiation, a maximum depth of approximately 2 microns (Coombs,1999).

The quality of spectra depended on intimate contact between the DurasamplIR reflection element (the diamond crystal had an active area of 1mm diameter) and the surface of interest. Identical pressure distribution was achieved for all samples using the flat, circular tip of the pressure device (3mm in diameter) supplied with the accessory in combination with the torque limiter which allowed the press to be tightened to the same, repeatable level. To ensure that the pressure applied during spectroscopic analysis was insufficient to squeeze DEHP to the surface, spectra were run of all model sheets under varying pressures including finger and the range available using the torque. No differences in the intensity of absorbance spectra were observed during the time required to scan each sample (30 seconds), providing that good contact between the diamond crystal and sample was achieved. Background spectra were collected from 30 scans of the empty, clean accessory open to air, at hourly intervals during examination of samples.

Spectra of DEHP, PVC powder used in Hydro and Solvay plastisols (donated by the two manufacturers), Eastman TXIB (donated by Bjørn Thorsen A/S, Copenhagen, Denmark), analytical grades of phthalic acid, phthalic anhydride and 2-ethylhexanol (Greyhound Chromatography and Merck) were run as references. Assignments made from these spectra for the most prominent bands of DEHP, Eastman TXIB and PVC bands are presented in Tables 5.7, 5.8 and 5.9.

Beer's Law, which specifies that spectral absorbance is proportional to the concentrations of two components in a mixture, was applied to the spectra. The two components of interest here were DEHP and the PVC polymer. Quantitative calculations required two independent absorbance bands, one attributed to a functional group in DEHP and another to a functional group in PVC. The absorbance band found at 1724 cm^{-1} , used by Dutta and Graf to quantify DEHP, was partly overlapped by a band at 1726 cm^{-1} assigned to the C=O stretch in Eastman TXIB, so could not be used to obtain independent data about the concentration of DEHP in Solvay model sheets (Figure 5.2 and 5.3). In addition, the region 1718-1800cm^{-1} contained the characteristic absorption frequencies for carbonyl-based oxidation and photodegradation products of PVC (Rabek, 1995).

Wavenumber cm^{-1}	**Molecular bond**	**Band character**
2858	C-H stretch	medium
1726	C=O	strong
1599	C-C due to aromatic ring	weak
1464	C-H	medium
1380	C-H	weak
1258	C-O	strong
1118	C-O	medium
1070	C-O	medium
1040	C-H	weak
741	C-H	medium

Table 5.7 Assignments for FTIR bands in spectrum of industrial grade DEHP used to plasticize Solvay and Hydro plastisols

Wavenumber cm^{-1}	**Molecular bond**	**Band character**
1732	C=O	strong
1470	C-H	medium
1258	C-O	strong
1068	C-O	medium
748	C-H	weak

Table 5.8 Assignments for FTIR bands in spectrum of Eastman TXIB

Wavenumber cm^{-1}	**Molecular bond**	**Band character**
1435	C-H amorphous	medium
1426	C-H crystalline	strong
1330	C-H twist	medium
1254	H-C-Cl bend	strong
959	C-H rock	medium
692	C-Cl	weak
637	C-Cl	medium
612	C-Cl	strong

Table 5.9 Assignments for FTIR bands in spectrum of PVC powder contained in Hydro and Solvay plastisols

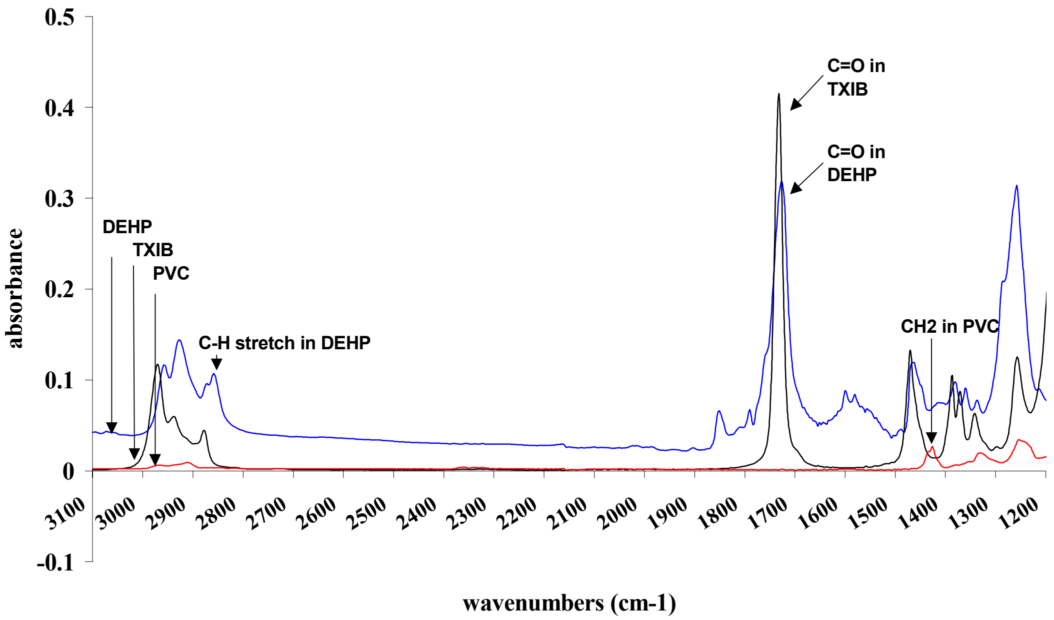


Figure 5.2 ATR-FTIR absorbance spectra of Eastman TXIB, DEHP and Solvic PVC powder used to prepare model sheets. C-H band for DEHP and CH stretch for PVC, used in quantitative measurements, are marked. The overlap between the positions of carbonyl bands of Eastman TXIB and DEHP is also shown.

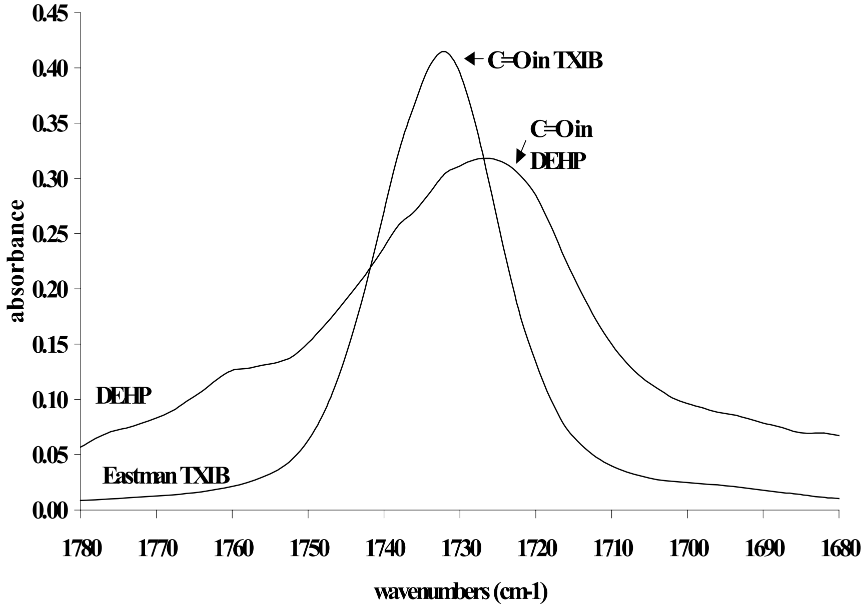


Figure 5.3 Overlap between positions of carbonyl bands for Eastman TXIB and DEHP

Instead, a band at 2860 cm^{-1} was assigned to the C-H stretch found only in the DEHP components of model sheets, and used for quantitative measurements (Tabb and Koenig, 1975). The concentration of the PVC component was obtained from the height of the band (absorbance intensity) at 1426 cm^{-1}, attributed to the CH_2 wagging of bonds in PVC and was not present in DEHP (Dutta and Graf, 1984). Concentrations of DEHP at sheet and 'object' surfaces were calculated by ratioing the heights of peaks at 2860cm^{-1} (C-H stretch, due only to DEHP) against those at 1426cm^{-1} (C-H stretch, due only to PVC) on raw absorbance spectra without manipulations or baseline corrections.

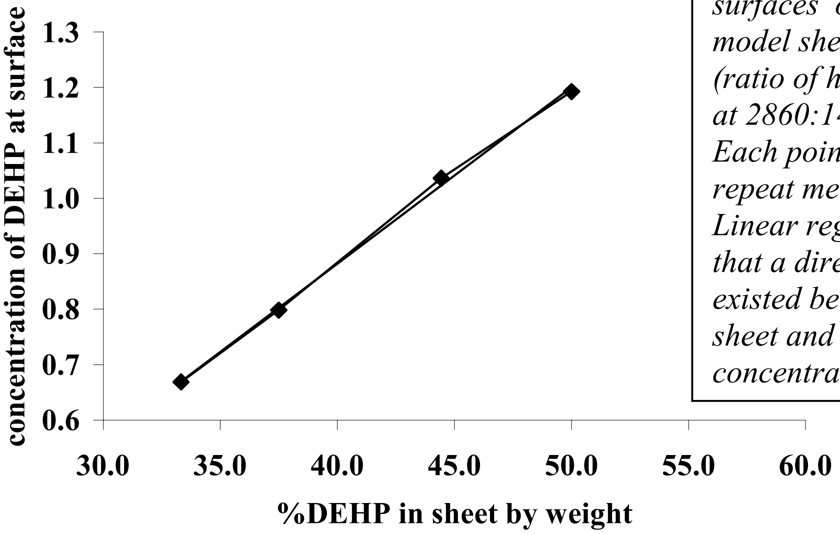


Figure 5.4
Concentration of DEHP at surfaces of unaged Hydro model sheets (ratio of height of FTIR band at 2860:1426 cm^{-1}). Each point represents ten repeat measurements. Linear regression showed that a direct relationship existed between %DEHP in sheet and surface concentration

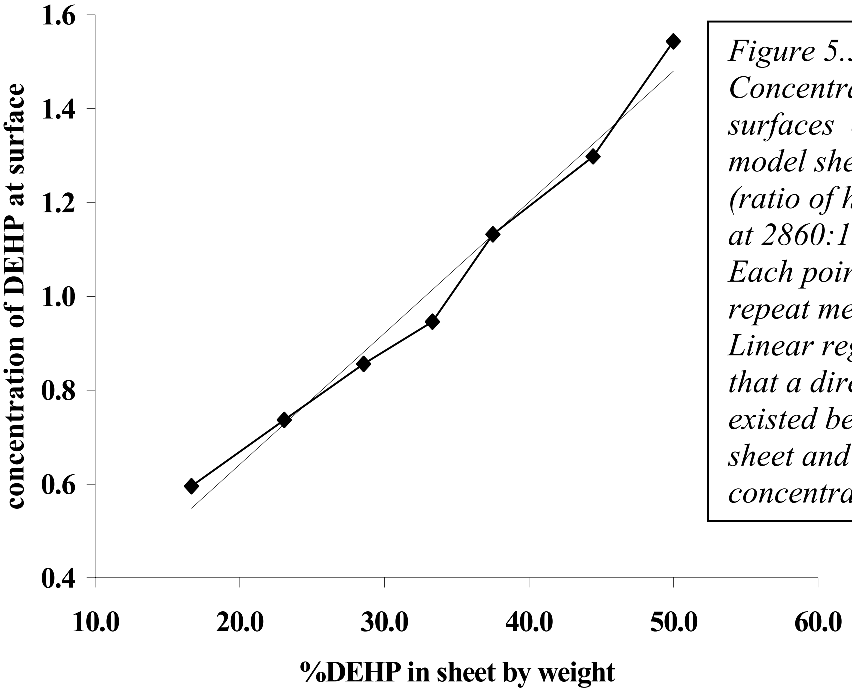


Figure 5.5
Concentration of DEHP at surfaces of unaged Solvay model sheets (ratio of height of FTIR band at 2860:1426 cm^{-1}). Each point represents ten repeat measurements. Linear regression showed that a direct relationship existed between %DEHP in sheet and surface concentration

Solvay sheets had higher DEHP concentrations (approximately by 0.3 concentration units) at the surface than Hydro sheets formulated with the same plasticizer level (Figures 5.4 and 5.5). Since the total plasticizer concentration of model sheets had been previously determined by Soxhlet extraction, and the DEHP concentration was known to be the same in both Hydro and Solvay sheets, this indicated a difference in plasticizer distribution between the two model sheets, perhaps due to the presence of Eastman TXIB in the Solvay formulation.

Discolouration of model sheets and objects

Densitometers are used in reflection mode as a standard method of measuring the degree of blackness or saturation in colour photographs after exposure and processing. They are also used in transmission mode to examine photographic negatives (Hendriks, 1991). A filter combined with a detector produces a spectral response similar to that of the human eye. To obtain data concerning the colour of a transparent sample, readings are taken through a set of filters.

Optical density is the common logarithm of the opacity, that is the ratio of the intensity of incident light to the intensity of transmitted light. Transparency, opacity and optical density are related as follows (Weast, 1979):

$$\text{Transparency} = It / Ii$$

$$\text{Opacity} = Ii / It$$

$$\text{Optical density} = \log_{10} (Ii / It)$$

where Ii = intensity of incident light
It = intensity of transmitted light

An electronic densitometer model Densy 301 from Barbieri was used to measure the optical density of model films and ‘objects’ in transmission mode. Samples were placed in clear, transparent Secol polyester sleeves to avoid contaminating the measuring head. The instrument was calibrated before each set of measurements to give a zero reading with a Secol sleeve in position. Since all colour changes were due to yellowing, a blue density filter from the Status A set was used. The mean reading at three positions of each sample was calculated.

When discoloration was uneven or presented as patches or spots, the approximate percentage area was determined using a simple method. The film was photocopied and the paper image weighed. The discoloured areas were cut out, weighed and the percentage calculated.

LV-SEM of model sheets and 'objects'

Scanning electron microscopy has not been widely used to examine plastics surfaces because high vacuum instruments, almost exclusively used until 5 years ago, require coating with carbon or gold to obtain a good image and analysis. Such treatments generate heat, which is likely to vaporize plasticizer and damage plastics surfaces due to their low Tg values. An extensive literature search found no references to previous use of LV-SEM applied to PVC.

A Jeol SM LV-5310 scanning electron microscope was used to examine the surface morphology and elemental composition of selected sheets and naturally aged 'objects' before and after thermal ageing. The principles and techniques of scanning electron microscopy and elemental analysis are described by Goldstein (1981). Samples (5x5mm) were adhered to aluminium stubs to examine their surface morphology. Since DEHP is readily absorbed by waxes, polyester and epoxy embedding resins, no mounting of sections was made to examine cross-sections. Instead, thin strips cut from model and naturally aged sheets (10x2x1mm) were trapped between two parallel glass microscope slides or aluminium sheets (when oxygen present in the structure of microscope slides was undesirable), so that they overhung by 3mm. A single, straight, vertical cut was made through each sheet using a microtome blade. No further preparation of sheets was necessary. The microscope slides or aluminium sheets were mounted vertically in the LV-SEM chamber, so that sheets could be examined end-on, parallel to the detector.

Samples were examined at magnifications of x150, x750 and x1500. Cross-sections were also mapped for distribution of elemental carbon, oxygen and chlorine. A beam current was maintained at 10KV and a spot size of 19 was used. Such low energy minimised damage to the samples which may have confused images and analyses.

6. Results and Discussion

Weight loss and headspace analysis

Since the fate of DEHP in plasticized PVC which has been exposed to various environments was the focus of interest in this project, the weight lost by model sheets was recalculated to express it as percentage plasticizer lost during ageing. Characterization of ethereal extracts from both Hydro and Solvay sheets by thin-layer chromatography and FTIR spectroscopy, suggested the presence of DEHP, as described in Chapter 5, 'Experimental methods'. In addition, Solvay films contained Eastman TXIB (2,2,4-trimethyl-1,3-pentanediol diisobutyrate) not present in Hydro films.

Expression of weight loss as percentage DEHP was based on the assumption that the volatile component from model sheets almost entirely comprised plasticizer, either DEHP (in Hydro model sheets and 'objects') or a blend of DEHP and Eastman TXIB (as in Solvay model sheets). Thin-layer chromatography had shown that plasticizers were the major low-molecular weight components and, therefore, likely to be the most volatile constituents of the model sheets. To show the actual mass of plasticizer lost by each sample in ageing environments, selected results were also presented as graphs of mean mass DEHP for Hydro and 'objects' or mass plasticizer blend (for Solvay samples) lost versus period of ageing. It should be remembered when looking at actual mass lost, that, although model sheets weighed approximately 1g before ageing, there was some variation between their initial masses.

DEHP loss from Hydro model sheets

The environment in which Hydro model sheets were aged, clearly influenced the extent and rate of loss of plasticizer during the 65-day period of ageing. Table 6.1 shows the ageing environments rated in increasing order of plasticizer loss resulting from a 65 day ageing period. Although the results presented are those for Hydro 33.3% model sheets, the rating applied to all Hydro sheets.

After completing the experimental ageing period, samples aged with silica gel, in an open oven, on an open glass plate and enclosed in a LDPE bag continued to lose weight. Samples in other ageing environments had stopped losing weight.

Hydro model sheets aged in high relative humidity (RH), freezer and closed environments lost less than 1% of the original plasticizer content, while those aged in open oven, on glass plate and in LDPE bags lost more than 5%, an amount which caused an increase in stiffness. There was very little difference between weight lost during ageing in a freezer and that lost in a closed microclimate at 70ºC for the same period of time, indicating that the storage temperature was a less important factor than the opportunity for plasticizer to migrate or evaporate.

Table 6.1 DEHP lost by Hydro 33.3% model sheets after accelerated thermal ageing for 65 days

accelerated ageing environment [1]	**% DEHP lost after 65 days (%)**	**mass DEHP lost after 65 days (g)**
high relative humidity **(lowest DEHP loss)**	0.0	0.000
freezer	0.4	0.002
closed	0.7	0.004
Ageless® oxygen absorber	3.0	0.015
silica gel	3.6	0.019
activated carbon	3.7	0.021
open oven	5.7	0.031
open glass plate	5.9	0.032
LDPE bags **(highest DEHP loss)**	10.1	0.044

[1] *all environments were maintained at 70°C with the exception of freezer (-20°C)*

Loss from sheets hanging in an open oven, with all surfaces available for evaporation was almost the same as that from sheets aged on open glass plates, despite the fact that the surface in contact with glass was not readily accessible by moving air to promote evaporation. However, DEHP was lost from the surface in contact with glass, observed by the presence of droplets between the underside of Hydro sheets and the glass. These droplets remained on the glass when sheets were removed for weighing, thereby contributing to the weight loss measurements.

Rate

Appendix A1 comprises graphs of %DEHP loss by all Hydro model sheets during periods of ageing in each environment. Graphs are presented in the same order as Table 6.1, that is environments causing least loss of DEHP (high RH) are presented first. With the exception of samples aged in freezer and high RH, curves suggested that loss was related to time of ageing for Hydro model sheets. The highest rate of DEHP loss took place within the first 7-10 days of the ageing period. After the intial rapid loss, DEHP was lost more gradually either at a rate proportional to time. In the case of closed environments and those containing activated carbon, loss of DEHP ceased after 14 days until completion of the ageing period, suggesting that the concentration of DEHP vapour in the air surrounding the model sheets and the concentration at their surfaces, had equilibrated. This was a good indication that the rate of loss was evaporation-controlled. Other researchers have also observed a similar type of initial rapid weight loss, followed by a linear period (Quackenbos, 1954).

The mass of DEHP lost from Hydro model sheets during ageing in closed environment (ageing environment causing low loss) and open oven (that causing higher loss) are presented in Appendix A1 for comparison. Loss of DEHP in closed environments was between 0.002g and 0.004g, and, in environments containing activated carbon, was between 0.011 and 0.015g from a 1g sample when evaporation ceased. These results suggested that activated carbon adsorbed very little DEHP from model sheets before the concentration of plasticizer vapour in the air and at the surface of model sheets were the same. The low adsorption by activated carbon may be partly attributed to the poor rate of ventilation in the ageing flasks which limited the access of activated carbon particles, located in the base of the flask, to DEHP vapour.

No droplets of condensed DEHP were observed on the walls of flasks during ageing, suggesting that the available airspace never became saturated with plasticizer vapour. A simple trial indicated that 10mL pure DEHP were required to produce condensation in the 100mL flasks used for the ageing experiments under the accelerated ageing conditions applied to model sheets and 'objects'(Figure 6.1). None of the model sheets or 'objects' contained such high amounts of DEHP, making it unlikely that condensation would take place in the experimental environments.

Figure 6.1
Approximately 10mL DEHP were required to produce droplets of condensation (visible between 60 and 80mL scale marks on flask) in a 100mL ageing flask at the accelerated ageing temperature applied to model sheets and 'objects'

Loss of DEHP from all Hydro model sheets aged in a freezer and, especially, at high RH environments occurred at varying rates during the ageing period. Hydro model sheets in high RH did not lose weight, but, in some cases, gained it, probably by adsorbing water vapour or liquid water from condensed vapour. This phenomenon has been formally recognised by other researchers. Martin and Johnson observed that poorly compatible plasticizers tend to detach from the PVC polymer allowing water vapour to migrate in, those plasticized with DEHP showed lowest weight gain (0.7%), suggesting its high compatibility. Less water vapour was adsorbed at high concentrations of plasticizer. This was explained by the fact that water vapour is an efficient plasticizer for rigid PVC (Martin and Johnson, 1974). After 65 days, Hydro model sheets containing 33.3% DEHP had gained more weight (0.005g) than those containing 50.0% plasticizer (0.0025g), thus confirming Martin and Johnson's observation.

Mechanism

Except for Hydro model sheets aged in closed, high RH and freezer environments, when loss was very low, samples containing 33.3% DEHP (the most lightly plasticized model sheet in this series) lost more plasticizer during ageing than those containing higher levels in all ageing environments. However, it was not possible to define such a pattern of DEHP loss for sheets containing other concentrations of DEHP. Several possibilities for this behaviour were investigated.

Small (Small, 1954) showed that percentage loss of plasticizer for a defined period was inversely proportional to sheet thickness for samples between 0.127 and 1.27mm containing 33.3% dibutyl phthalate. Hydro model sheets had thicknesses between 0.53 and 0.55mm, fitting the specified range, although the difference in thickness between Small's sheets was 90% compared with a relatively insignificant difference of 4% for those prepared for this project. According to the 'inverse proportionality' theory fitted data from the Hydro sheets, DEHP should be lost in the following order:

Hydro 50.0%	(0.53mm-should lose most DEHP)
Hydro 44.4%	(0.55mm)
Hydro 33.3%	(0.56mm)
Hydro 37.5%	(0.57mm-should lose least DEHP)

However, this order did not fit the observed pattern of weight loss from Hydro model sheets in any ageing environment.

The possibility of thermodynamic incompatibility between DEHP and PVC was also considered. Such incompatibility may make loss of DEHP more energetically favourable at some levels of plasticization than others. All published thermodynamic measurements suggested that lower concentrations of DEHP are more compatible with PVC than higher ones. This was the opposite trend to that observed for the Hydro model sheets.

Another factor in the rate of loss is permeability of the model sheets. When loss of DEHP vapour from the surface is rapid, diffusion of DEHP from the bulk to the surface becomes the rate-determining step of plasticizer loss. The rate of diffusion is related to the plasticizer's molecular size and shape and to the permeability of the PVC. Permeability is strongly influenced by plasticizer level, diffusion being slower through a lightly plasticized formulation than through a more open structure given by high plasticizer levels. Again, this was the opposite trend to that observed, so was discounted.

Evaporation-controlled loss is linear with time and independent of plasticizer content, it depends only on sufficient difference between the concentration of DEHP vapour in air above the sheet and at the surface of the sheet itself to drive evaporation (Wilson,1995). The plasticizer content is not a factor in the rate of evaporation, so long as there is less DEHP in the airspace above the sheet than at the surface of the sheet. This was the most likely explanation for the observed trend.

Plasticizer loss from Solvay model sheets

The environment in which Solvay model sheets were aged, influenced the extent and rate of loss of plasticizer during the 65-day period of ageing. In comparison to Hydro sheets, Solvay sheets contained Eastman TXIB plasticizer in addition to DEHP. Eastman TXIB was known to be twice as volatile as DEHP under the same conditions. Since DEHP alone had been used to dilute the Solvay plastisol and produce the series of model sheets, the percentage of TXIB decreased from 16.7% in Solvay 16.7% to 10% in Solvay 50.0%.

Table 6.2 shows the ageing environments rated in increasing order of plasticizer loss resulting from a 65 day ageing period. Although the results presented are those for Solvay 16.7% model sheets, the rating applied to all Solvay sheets.

Table 6.2 Weight loss expressed as both DEHP and total plasticizer lost by Solvay 16.7% model sheets after accelerated thermal ageing for 65 days

accelerated ageing environment [1]	**% DEHP lost after 65 days (%)**	**% total plasticizer (DEHP + Eastman TXIB) lost after 65 days (%)**	**mass total plasticizer lost after 65 days (g)**
closed **(lowest loss)**	5.8	3.0	0.015
freezer	7.2	4.2	0.018
high RH	21.0	22.4	0.090
Ageless® oxygen absorber	58.0	29.1	0.110
silica gel	91.2	46.0	0.185
activated carbon	98.9	49.4	0.280
LDPE bags	122.0 [2]	60.4	0.270
open glass plate	128.0 [2]	64.6	0.440
open oven **(highest loss)**	128.0 [2]	64.8	0.450

[1] *all environments were maintained at 70°C with the exception of freezer (-20°C)*
[2] *results indicate that weight loss corresponded to more than 100% loss of DEHP*

Although many similar trends in effect of environments on loss of DEHP were seen between Solvay and Hydro model sheets, the loss of plasticizer from Solvay samples was approximately ten times higher than for a Hydro sheet containing the same percentage of total plasticizer. For example, Solvay 16.7% model sheets contained 33.4% DEHP plus Eastman TXIB, almost the same level of plasticizer as Hydro 33.3%, but the former lost considerably more weight under the same ageing conditions for the same period of time. Since the major difference between Solvay and Hydro formulations was the presence of Eastman TXIB, the increased weight loss was likely to be due to the co-plasticizer.

Solvay samples aged in LDPE bags, on open glass plates or in open oven, lost more weight than that corresponding to 100% DEHP. This strongly indicated a substantial loss of another volatile material present in the Solvay formulation in addition to that of DEHP. Since it evaporated twice as fast as DEHP under the same conditions, Eastman TXIB was the most likely cause of the high loss.

Rate

Appendix A2 comprises graphs of %DEHP loss by all Solvay model sheets during periods of ageing in each environment. Graphs are presented in the same order as Table 6.2, that is the environment causing least loss of DEHP (closed) is presented first.

Solvay sheets containing lower concentrations of DEHP, lost a greater percentage of their original weight than those containing higher levels, during the same period of time in all environments. This may not be directly attributed to the concentration of DEHP, but to the decreasing levels of Eastman TXIB on going from Solvay 16.7% (also contained 16.7% TXIB) to Solvay 50.0% (also contained 10% TXIB). Since Eastman TXIB has a lower vapour pressure and higher volatility than DEHP (boiling point was 280ºC for TXIB compared with 386°C for DEHP), the former plasticizer was expected to be lost at an earlier stage of ageing. Vapour pressure data was not available for Eastman TXIB. An exception in these trends was observed when model sheets were aged either in closed microclimates or a freezer. Such environments caused all Solvay sheets to lose similar, low weight percentages.

As for Hydro samples, the pattern of Solvay sheets containing lower concentrations yet losing more plasticizer than those containing higher concentrations did not fit with Small's findings that loss of plasticizer was inversely proportional to sheet thickness (Small, 1954).

Only storage in closed environments and in freezer for 65 days caused loss of plasticizer lower than 10-12% from all Solvay model sheets. This is considered to be the point at which plasticized PVC reaches the end of its useful life for industrial application (Quackenbos, 1954). All other ageing environments caused loss higher than 22%. Loss from sheets hanging in an open oven, with all surfaces available for evaporation was almost the same as that from sheets aged on open glass plates, despite the fact that the surface in contact with glass was not readily accessed by moving air to promote evaporation. However, plasticizer was lost from the surface in contact with glass, observed by the presence of droplets between the underside of Solvay sheets and the glass. These droplets remained on the glass when sheets were removed for weighing, thereby contributing to the weight loss measurements.

Mechanism

Ageing environment also influenced the mechanism by which weight was lost. Solvay sheets exhibited both multistage and single stage weight loss mechanisms. Multistage mechanisms were defined by alternating periods of high weight loss and periods during which almost no weight was lost and equilibrium appeared to have been reached. This pattern was repeated at least twice during the ageing period of this study. Single stage mechanisms were defined by a single period during which weight was lost after which equilibrium was attained.

Solvay sheets followed a multistage weight loss mechanism when aged in a freezer, in high relative humidity, enclosed with Ageless oxygen absorber, on open glass plate, in open oven or in LDPE bag. The most likely explanation for such a mechanism was associated with the presence of Eastman TXIB. The plasticizer has a lower vapour pressure than DEHP and, therefore, evaporated early in the ageing process. When most of the TXIB had evaporated, there was a period (shown as the plateau on the graphs) in which little volatile material was available at the surface of the model sheet for evaporation. The second period of weight loss was due to the evaporation of DEHP.

Plasticizer loss curves for Solvay model sheets aged in the same environment, flattened, that is they assumed an increasingly linear shape as films increased in concentration of DEHP from 16.7% to 50.0%. This may be explained by the fact that Solvay sheets with higher levels of DEHP had progressively lower concentrations of TXIB. As a result, the first periods of weight loss, due to TXIB, became less intense and were not so readily distinguished from the plateau and second period of loss due to DEHP.

The mass of DEHP lost from Solvay model sheets during ageing in closed environment (the ageing environment causing least loss) and open oven (that causing higher loss) are also presented in Appendix A2 for comparison. Solvay sheets lost weight following a single stage mechanism when aged with activated carbon, silica gel and in a closed microclimate. Loss of plasticizer ceased after approximately 35 days and losses of 0.290g (activated carbon), 0.184g (silica gel) and 0.011g (closed) from Solvay 16.7% sheets had occurred. In the latter environment, it was likely that following a period when TXIB/DEHP evaporated from the surface of the sheet, the air close to the surface of the model sheet became saturated with plasticizer vapour. Since there was minimal movement of air, the concentration gradient in this area remained close to zero, and further loss from the sheet was inhibited. It is unlikely that silica gel and activated carbon were saturated with volatiles, but their uptake of plasticizer was limited by temperature and by accessibility to TXIB/DEHP molecules in the poorly agitated ageing environments used. The only source of air movement inside the closed flasks was due to convection caused by small temperature (measured as less that 1ºC) variations of the air in the oven.

Weight loss from 'objects'

Since the original formulation and, in particular, the levels of plasticizer, in the two naturally aged 'objects' were not accurately known, it was not possible to quantify percentage of plasticizer lost. Instead, results were expressed as percentage weight lost during ageing in different environments .

As for model sheets, the environment in which 'objects' were aged, influenced the extent and rate of loss of volatiles during the 65-day period of ageing. The percentage of weight lost, increased in the order shown in Table 6.3.

Table 6.3 Weight loss from 'objects'

environment	**% weight lost by tube after 65 days (%)**	**% weight lost by microscope cover after 65 days (%)**
high relative humidity **(lowest % weight loss)**	0.0	0.0
closed	0.0	0.2
freezer	0.2	0.1
Ageless oxygen absorber	0.4	0.8
silica gel	0.4	1.4
activated carbon	0.6	1.6
open oven	1.6	1.6
open glass plate	1.7	2.6
LDPE bags **(highest % weight loss)**	1.9	2.8

Rate

Appendix A3 comprises graphs of percentage weight loss by 'objects' during periods of ageing in each environment. Graphs are presented in the same order as Table 6.3, that is the environment causing least loss (high RH) is presented first. Environments affected the weight loss of both 'objects' similarly; those environments which promoted weight loss from the tube also caused loss of volatile material from the microscope cover. Effects of environments on weight lost by 'objects' were similar to those on plasticizer loss from model sheets, despite the fact that samples of tube were considerably thicker than model sheets or microscope cover.

Samples of microscope cover lost more weight than tube samples in all environments during the same period of ageing, although neither material lost more than 0.1g. Percentage weight losses from both 'objects' were lower than those from Hydro model sheets, so that the rate of loss during the experimental period was slower for 'objects'. This was attributed to the fact that during their 15-20 year period of natural ageing, some plasticizer and other volatile materials had already been lost. Samples aged in open oven, on open glass plate and in LDPE bags lost weight rapidly in the first 10 days of ageing before the rate of loss slowed.

Mechanism

With the exception of samples aged in freezer and high RH, smooth curves were obtained by plotting percentage weight loss against period of ageing. After the intial rapid loss, percentage weight lost was directly proportional to ageing time, excepting samples in freezer and high RH, a good indication of loss by evaporation .

Conclusions from weight loss of model sheets and ‘objects’

It was concluded that percentage DEHP loss from all model plasticized PVC samples and percentage weight loss from both ‘objects’ increased in the following order of environment types (Table 6.4) :

Table 6.4 Influence of storage environment on loss of plasticizer from PVC

storage environment category	**examples**
enclosed with still, unstirred air **(lowest loss of plasticizer)**	freezer, closed, high relative humidity
enclosed with adsorbent materials in the same air space	Ageless oxygen absorber, silica gel, activated carbon
lightly stirred air	open oven, open glass plate
enclosed in contact with highly adsorbent material **(highest loss of plasticizer)**	LDPE bags

To compare the effect of each environment in a quantitative way, the time taken for model sheets to lose 10% of weight in each environment was calculated. As stated previously, in industrial research, a vinyl sheet that has lost 10% of its weight is considered to have changed so much in character that such a loss represents failure. To present a ‘worse case scenario’, Solvay model sheets containing 16.7% and 50.0% DEHP were used in the calculation, since they lost weight more rapidly than Hydro model sheets.

The time for both model sheets to lose 10% weight in all ageing environments was determined from the weight loss measurements. Loss of DEHP and other plasticizers has been shown to follow the well-known rule of thumb which states that loss doubles for every 10°C change in temperature (Wilson, 1995). On the basis that accelerated ageing was carried out at 70°C, with the exception of freezing, the time for 10% weight to be lost from the two model sheets was calculated (Table 6.5). Since it is questionable whether model sheets stored in freezer, closed environment or at high RH can lose as much as 10% by weight, the extrapolation of time to lose 10% is a conservative estimate for those environments. It is clear from this approximation that the useful lifetime of plasticized PVC objects may be significantly extended from less than one year to more than 11 years, in the case of a lightly plasticized material, and from 1.25 years to 11.4 years for a highly plasticized material, by changing the storage environment from a polyethylene bag to a closed glass container or by placing the object in a freezer.

Table 6.5 Comparison of time required for Solvay model sheets to lose 10% original weight in various thermal ageing environments

environment	**Solvay 16.7% measured time to lose 10% wt at 70° C (days)**	**Solvay 16.7% predicted time to lose 10% wt at 20°C (days)**	**Solvay 50.0% measured time to lose 10% wt at 70° C (days)**	**Solvay 50.0% predicted time to lose 10% wt at 20 °C (days)**
LDPE bag	4	256	7	448
open glass	4	256	30	1920
open oven	5	320	8	512
activated carbon	5	320	60	3840
silica gel	9	576	42	2688
Ageless oxygen absorber	33	2112	65	4160
freezer **closed** **high RH**	>65	>4160	>65	>4160

Analysis of volatiles produced by model sheets and 'objects'

Headspace analysis using GC-MS was used to identify the gaseous organic components in the atmosphere inside the flasks during thermal ageing. Due to its invasive nature, long measurement time and the practical problems associated with condensation of samples between collection from flasks at 70°C and transfer to the gas chromatograph/mass spectrometer for analysis, it was used only to investigate samples before and after ageing in closed and activated carbon environments. The chromatograms obtained for samples were compared with those of reference samples run on the same equipment.

The chromatogram shown (Figure 6.2) represents those obtained for all Solvay samples after closed ageing and ageing with adsorbents for 65 days. It identifies the presence of Eastman TXIB, DEHP and alkyl benzenes. These were the only compounds identified in the airspace above aged Solvay model films. No Eastman TXIB was detected in the airspace above Hydro model sheets, only DEHP and alkyl benzenes. Alkyl benzenes, such as 1-methylpropyl benzene are documented as commonly-used stabilizers included in PVC formulations (Sears and Darby, 1982). No degradation products from DEHP or PVC were detected.

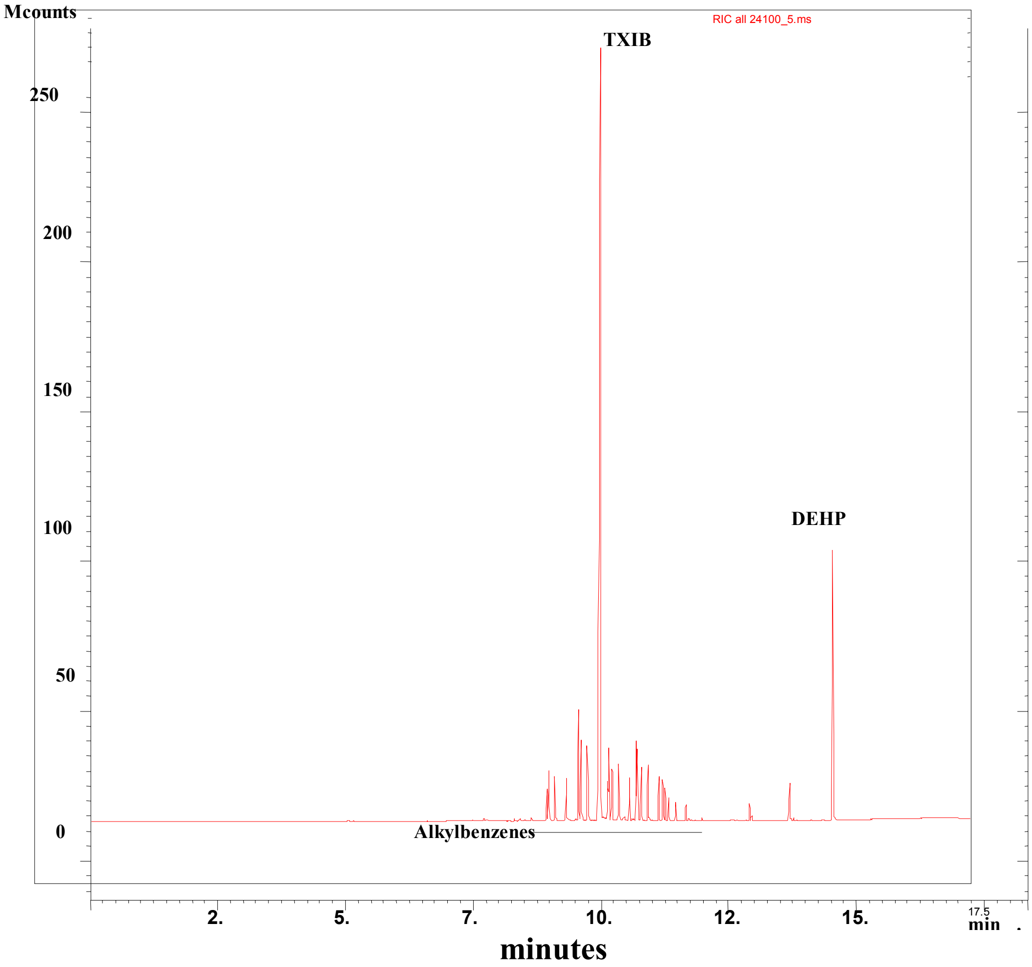


Figure 6.2 Gas chromatogram of vapour mixture above Solvay 33.3% after 65 days accelerated thermal ageing in a closed environment

Universal indicator paper was used to identify any hydrogen chloride produced as a result of PVC degradation in a closed flask. Model sheets did not produce a change in colour for the indicator paper, regardless of environment. By contrast, samples of microscope cover and tube aged with activated carbon or with silica gel, caused indicator paper to become either tan-coloured (indicative of pH 4) or dark yellow (pH 3). The results suggested that the PVC polymer components of ‘objects’ degraded during ageing with the two adsorbents.

Attenuated Total Reflection-Fourier transform infrared (ATR-FTIR) spectroscopy

No major products, such as phthalic acid or phthalic anhydride resulting from the degradation of DEHP, were identified at the surfaces of model sheets on ageing in the experimental environments (Figures 6.3 and 6.4). This suggested that the conditions in which samples were aged may have promoted the migration, but not the breakdown of plasticizer during the period of ageing used.

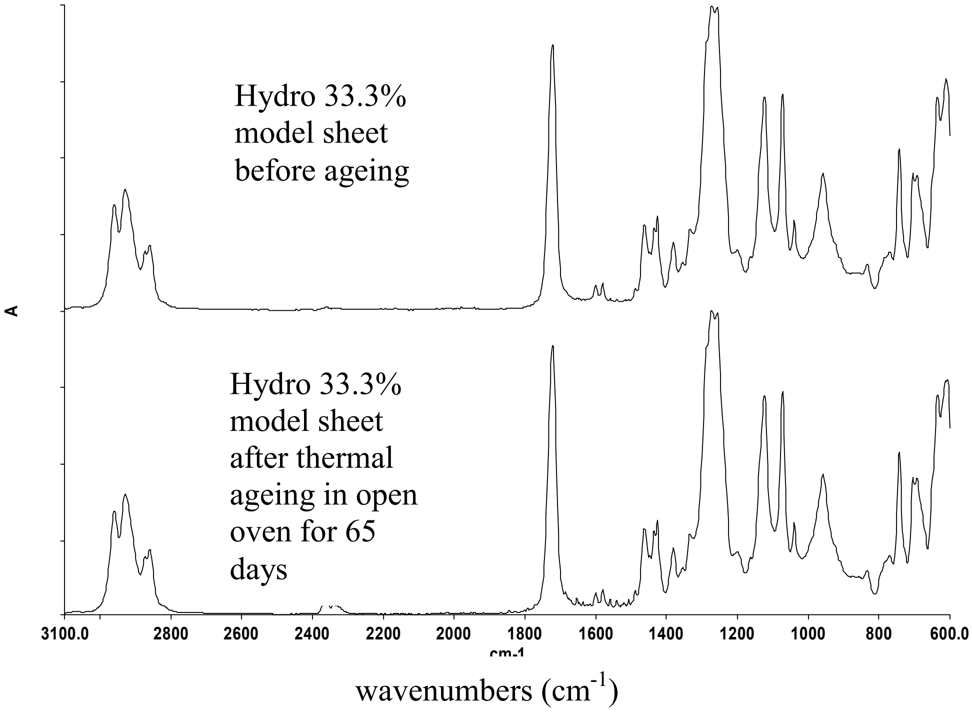


Figure 6.3 ATR-FTIR absorbance spectra of Hydro 33.3% before (upper) and after ageing at 70°C in an open oven for 65 days (lower). No change in position of absorbance bands has taken place during ageing, only a change in absorbance intensity

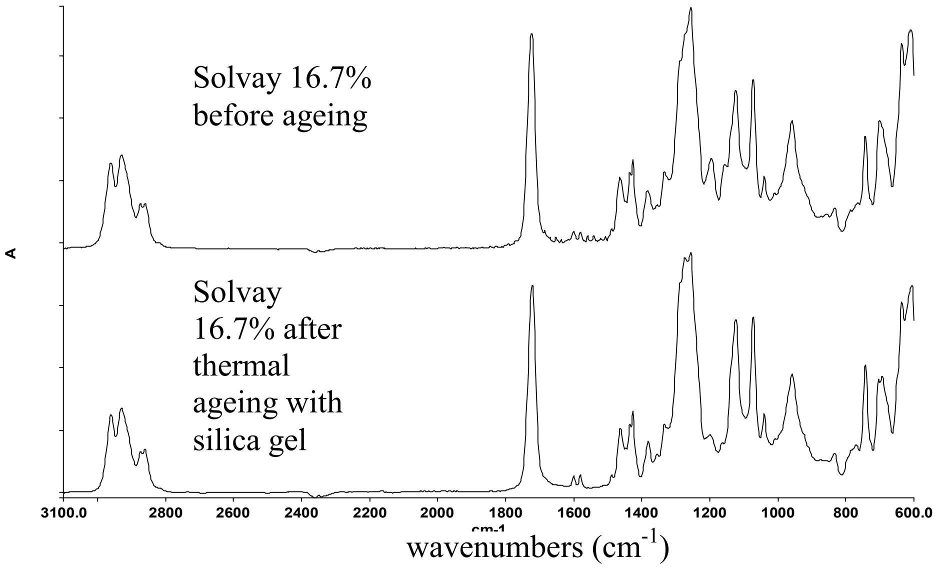


Figure 6.4 ATR-FTIR absorbance spectra of Solvay 16.7% before (upper) and after ageing at 70°C with silica gel for 65 days. No change in position of absorbances bands has taken place during ageing, only a change in absorbance intensities .

Concentration of DEHP at surfaces of model sheets and ‘objects’

ATR-FTIR spectroscopy was carried out immediately after weight loss measurements for all samples at weekly intervals during the ageing process. Concentrations of DEHP at sheet and ‘object’ surfaces were calculated by ratioing the absorbance intensities of peaks at 2860cm^{-1} (C-H stretch, due only to DEHP) against those at 1426cm^{-1} (C-H stretch, due only to PVC) on raw absorbance spectra without manipulations or baseline corrections. The relationships between concentration of DEHP at surfaces and percentage DEHP in unaged model sheets are presented in Chapter 5, ‘Experimental methods’, (Figures 5.4 and 5.5).

Concentration of DEHP at surfaces was plotted against period of ageing in each environment for model sheets and ‘objects’ to examine the rate of any changes with time. Appendices B1 and B2 comprise graphs of concentration of DEHP at surfaces during ageing for Hydro and Solvay model sheets respectively. They are presented in order of environments causing increasing loss of DEHP. To assist comparison between the effect of ageing in different environments for ‘objects’, concentration of DEHP at the surface before and after ageing in all environments for 65 days was presented as bar charts (Figure 6.5).

Since the surface concentration values represented the mean of five measurements, each of which comprised 30 scans, taken at random positions on both upper and lower surfaces of aged model sheets and ‘objects’ (ten measurements in total) the level of significance was determined using a t-distribution statistical test (Miller and Miller, 1993). Mean concentrations of DEHP at the surfaces of aged model sheets and ‘objects’ were compared with those measured for unaged samples to establish whether a minimum 95% confidence interval between the mean values existed. If not, it was concluded that there was no significant difference in the surface concentration of DEHP before and after ageing for 65 days.

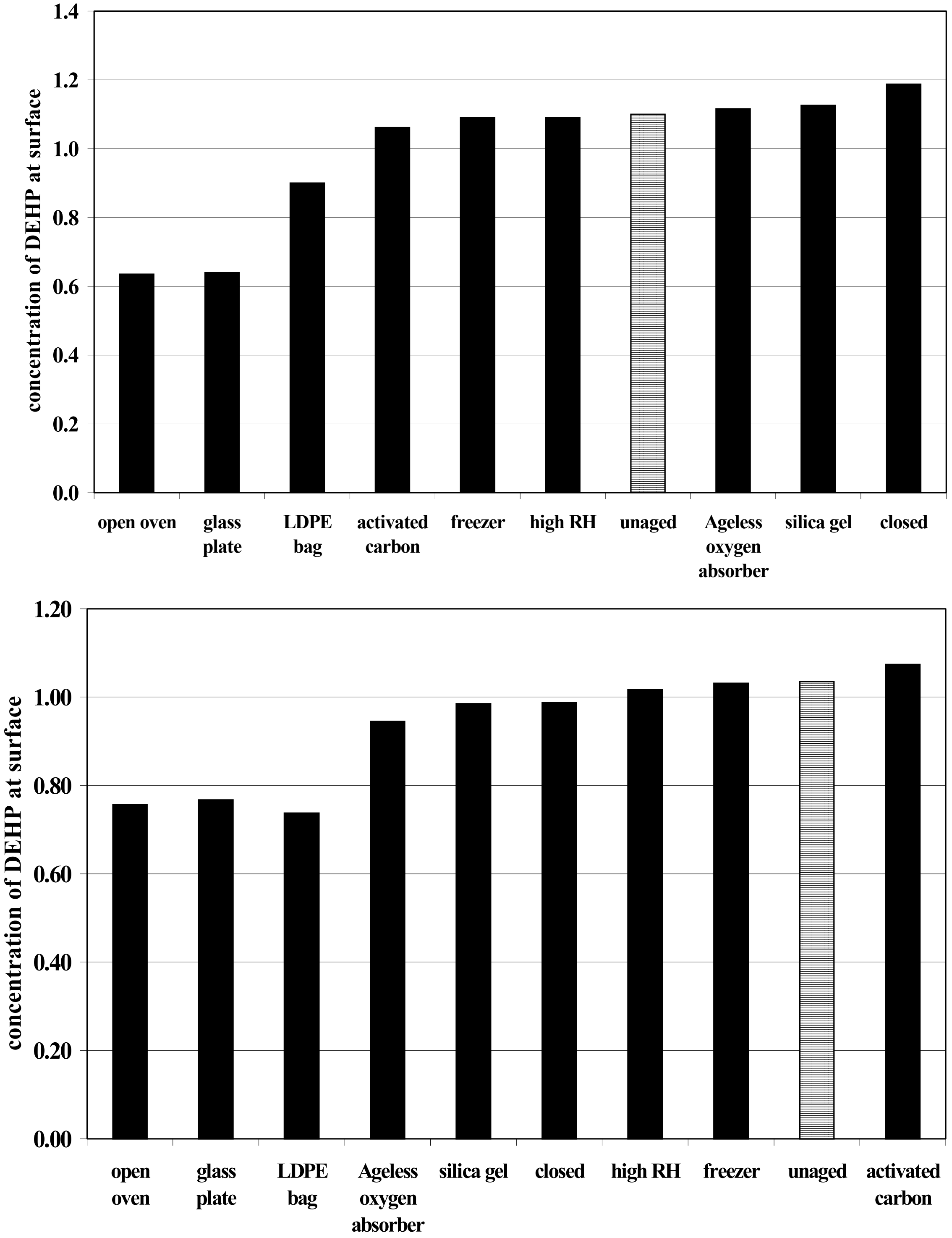


Figure 6.5 Concentration of DEHP at surfaces of microscope cover (upper) and tube (lower) before ageing (striped bars) and after 65 days accelerated thermal ageing

DEHP at surfaces of Hydro and Solvay model sheets on ageing

Based on the t-distribution, it was concluded that only ageing in open oven, on open plate and in LDPE bags significantly reduced the surface concentration of all Hydro and Solvay model sheets . In all other environments, sheets retained their original surface concentrations throughout the ageing period.

This suggested that during ageing in closed environments, freezer and with adsorbents, plasticizer at the surfaces of model sheets aged was replaced at the same rate as it was lost, by diffusion from the bulk of the sheet. As a result, no change in surface concentration was detected; evaporation was the rate-determining step by which DEHP was lost. By comparison, loss of DEHP from the surface of Hydro and Solvay model sheets during ageing in an open oven, on open glass plate and in LDPE bags occurred too rapidly for it to be replaced immediately by diffusion. As a result, a significant reduction in the surface concentration was measured and diffusion became the rate-determining step of the loss process.

Rate

Regression analysis suggested that the concentration of DEHP at the surface of Solvay model sheets showed good linear correlation with period of ageing in all environments. Where DEHP was lost from the surface it occurred slowly (Table 6.6). Both Hydro and Solvay model sheets lost DEHP from their surfaces at similar rates during the 65 day ageing period.

Table 6.6: Rate of loss of DEHP from the surface of model sheets and objects during ageing in open oven, on open glass plate and in LDPE bags

Rate of loss of DEHP from surface (concentration units per day)

	open oven	open glass plate	LDPE bags
Hydro model sheets	0.001- 0.003	0.001- 0.004	0.001- 0.003
Solvay model films	0.003 –0.004	0.001-0.003	0.002- 0.003
microscope cover	0.004	0.002	0.003
tube	0.004	0.004	0.004

DEHP at surfaces of 'objects' on ageing

Microscope cover

ATR-FTIR spectroscopy showed that samples of unaged microscope cover had a mean DEHP concentration of 1.1 concentration units at its surfaces (Figure 6.5). The formulation was considered to be more similar to that of Hydro than to Solvay model sheets since FTIR spectroscopy did not detect the presence of co-plasticizer Eastman TXIB. Fitting this value to the calibration curve obtained for unaged Hydro model sheets, suggested that the surface concentration of DEHP corresponded to a bulk concentration of 46.5% (Figure 6.6).

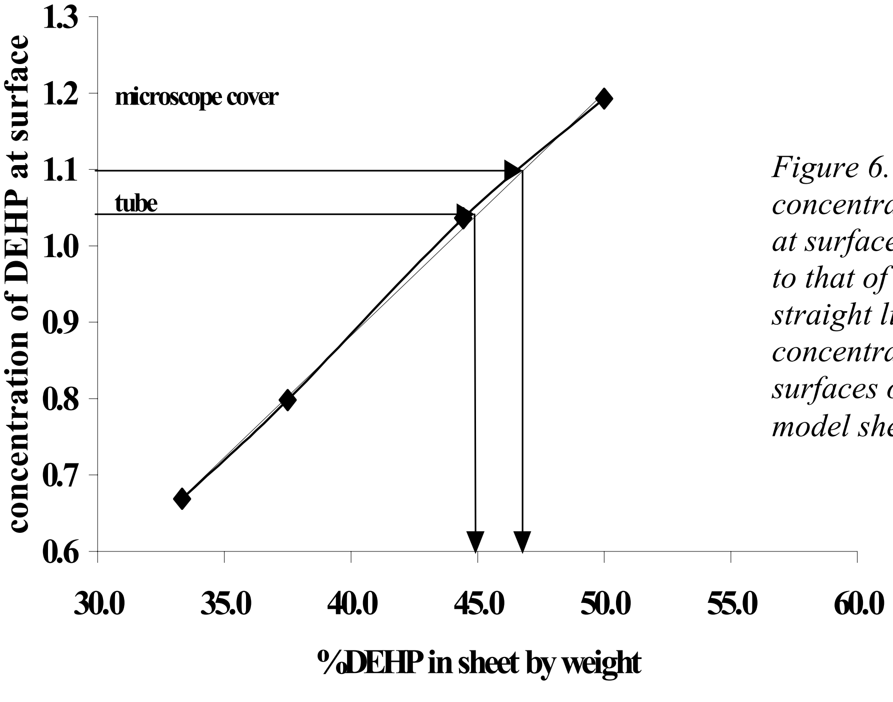


Figure 6.6 Fitting concentration of DEHP at surfaces of 'objects' to that of the best straight line for concentrations at surfaces of Hydro model sheets.

Based on the t-distribution, it was concluded that only ageing in open oven, on open plate and in LDPE bags significantly reduced the surface concentration of DEHP for the microscope cover. All other environments enabled the microscope cover to retain its original surface concentration throughout the ageing period. As described previously for the model sheets, these results indicated the presence of two mechanisms by which DEHP was lost. The rate-determining step by which DEHP was lost during ageing in a freezer and with adsorbents was evaporation. However, loss of DEHP from the surface of the microscope cover during ageing in an open oven, open glass plate and in LDPE bag occurred too rapidly for it to be replaced immediately by diffusion. As a result, a reduction in the surface concentration was detected and diffusion became the rate-determining step of the loss process.

Loss of DEHP from the surface of the microscope cover was compared with that lost by Hydro 44.4% and Hydro 50.0% model sheets after ageing in experimental environments, since all three materials contained similar levels of plasticizer prior to ageing. After ageing, the extent and rate of loss of DEHP from the surface of the microscope cover were similar to that of the equivalent model sheets (Table 6.6).

Tube

ATR-FTIR spectroscopy suggested that samples of unaged tube had a mean concentration of 1.04 concentration units at its surfaces (Figure 6.5). This value was fitted to the calibration curve obtained for unaged Hydro model sheets. It corresponded to a bulk concentration of 44.8% DEHP (Figure 6.6).

Applying the t-distribution to the surface concentration measurements, it was concluded that only ageing in open oven, on open plate and in LDPE bags significantly reduced the surface concentration of DEHP for the tube. After ageing in all other environments the ‘object’retained its original surface concentration throughout the ageing period. The mechanisms by which DEHP were lost were as described previously for the microscope cover.

Loss of DEHP from the surface of the tube was compared with that lost by Hydro 44.4% model sheet after ageing in experimental environments. In the same period of ageing , extent and rate of loss of plasticizer from the surface of the tube was similar to that of the equivalent model sheet. For example, ageing in a LDPE bag for 65 days resulted in a reduction of 0.1 concentration units for Hydro 44.4% model sheet; the same conditions produced a reduction of 0.3 units for the degraded tube.

Change in crystallinity on freezing

Although freezing of model sheets and ‘objects’ was shown to preserve original surface concentration of DEHP at the surfaces, there was some concern that the process might increase crystallinity of the PVC polymer. The freezing points of the two plasticizers present in model sheets, DEHP and Eastman TXIB were –47°C and -70°C respectively, so it was unlikely that they would be affected by storage at the temperature of a domestic freezer (-20°C). Crystalline regions of PVC polymer are not solvated by plasticizers, which tend to associate with amorphous regions.

The methylene deformations at 1435 and 1427cm^{-1} have been assigned as amorphous and crystalline bands for PVC respectively (Tabb and Koenig,1975). The bands were small and partially overlapping in spectra of Solvay and Hydro model sheets and ‘objects’ but it was possible to measure the heights of both on the same raw absorbance spectra used to determine the concentrations of DEHP before and after freezing (Figure 6.7). The ratio of the height of the band at 1427cm^{-1} was ratioed against that at 1435cm^{-1}, and the t-test applied as described previously to establish whether a minimum 95% confidence interval between the mean values before and after freezing existed.

Only the microscope cover and tube showed a small (2.1 and 3.2% respectively) but significant increase in crystallinity on freezing. This increase was reversed after 30 days at ambient conditions.

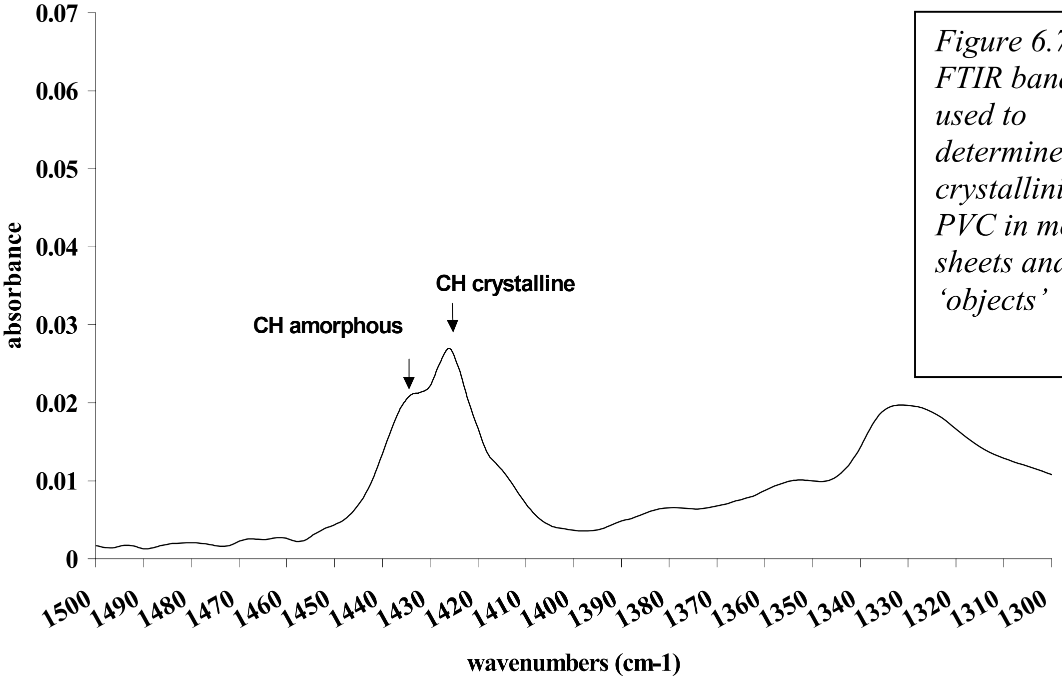


Figure 6.7 FTIR bands used to determine crystallinity of PVC in model sheets and 'objects'

Discolouration and tackiness of surfaces

Discolouration and tackiness of Hydro model sheets

Hydro model sheets were slightly yellow and transparent immediately after preparation and conditioning, suggesting that there had been insufficient thermal stabilizer in the plastisol formulation to render them water-white. Ageing in some environments caused sheets to develop a yellow or brown colouration, it was always evenly distributed. The differences between mean optical density for unaged sheets and the maximum optical density measured after 65 days in each environment were calculated, and are presented in Table 6.7. The presence of tackiness at the surfaces of films is also shown.

In the table, environments are ranked in order of that having least effect on optical density of aged samples (first in table) to that having greatest effect (last in table). Total increase in optical density for all Hydro model sheets aged in a particular environment was calculated; the total was used to rank environments.

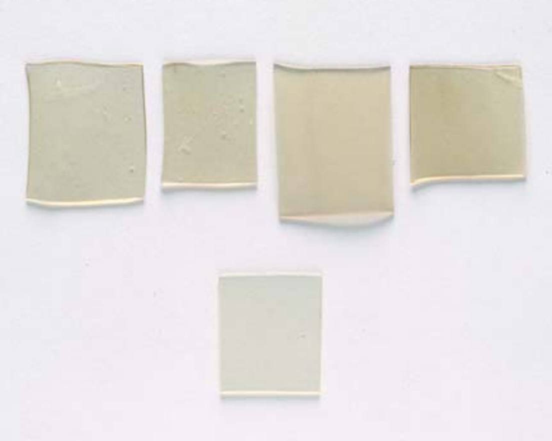
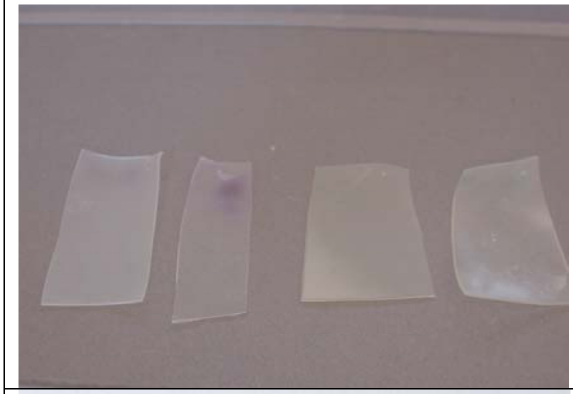
Table 6.7 Change in appearance and tackiness of Hydro model sheets after ageing

Key to table	
upper number	**-increase in optical density**
lower letter	**-'T' denotes sample had tacky surfaces**

Increase in optical density after 65 days in ageing environment

environment	**Hydro 33.3%**	**Hydro 37.5%**	**Hydro 44.4%**	**Hydro 50.0%**
closed	0	0	0 T	0 T
high RH	0	0	0	0
freezer	0	9	1 T	0 T
Ageless oxygen absorber	0	1	1 T	1 T
activated carbon	5 T	3 T	1 T	1 T
open oven	2	10	0 T	1 T
open glass plate	3 T	11 T	1 T	0 T
LDPE bags	8 T	7 T	4 T	0 T
silica gel	3	9	7 T	7 T

In general, where discolouration occurred, Hydro sheets containing lower concentrations of DEHP exhibited greater change in optical density than more highly plasticized samples. Ageing in a closed environment produced no change in optical density, while ageing in LDPE bags and silica gel produced unacceptable darkening of sheets, particularly for less plasticized sheets. When discolouration occurred, it was visible first at the edges of the sheets (approximately 0.5mm thick) before it was observed at the surfaces (Figures 6.8 and 6.9).

	*Figure 6.8* *Hydro model sheets before (bottom row) and after 65 days accelerated thermal ageing with Ageless oxygen absorber. Although discolouration was minimal, it appeared greatest at the edges of sheets. Sheets containing least DEHP (from right to left sheets contained 33.3%, 37.5%, 44.4%, 50.0%) discoloured more than those containing most.*
	*Figure 6.9* *Hydro model sheets before (bottom row) and after 65 days accelerated ageing with activated carbon. From right to left sheets contained 33.3%, 37.5% 44.4%, 50.0% DEHP. Edges of sheets appeared darker than the bodies.*
	*Figure 6.10* *Hydro and Solvay model sheets became opaque after ageing at high RH for 65 days. Less plasticized formulations achieved higher opacity. From right to left, sheets are Hydro 50.0%, Hydro 33.3%, Solvay 50.0%, Solvay 16.7%. Original transparency was regained after dehydration.*
	*Figure 6.11* *LDPE bags softened and crinkled after adsorbing plasticizer during use as accelerated thermal ageing environments for model sheets and 'objects'. Plasticizer may be seen in the lower third of both bags as a matte area.*

Ageing at high RH caused sheets to appear cloudy or white and opaque. Discrete droplets of plasticizer were visible at the surface. However, after removing sheets from the environment and allowing them to dehydrate fully, very little change in the original optical density was visible. After removal from the ageing environment, sheets containing higher levels of DEHP dehydrated more rapidly than less plasticized samples (Figure 6.10).

The hydration and dehydration of PVC plasticized with DEHP has been studied by Mura et al. using FTIR spectroscopy (Mura, 2001). They found that less water was taken up by PVC discs containing increasing levels of DEHP and suggested that either polymer-water interactions or water-DEHP interactions created site exclusion thereby preventing sorption of water. Another possibility was that there was a decrease in solubility of water in the PVC as the relatively hydrophobic DEHP concentration increased. The results obtained in the present research fitted those published; if less water was adsorbed by the more highly plasticized Hydro model sheets, dehydration would be expected to occur more rapidly in Hydro 50.0% than Hydro 33.3%. These expectations were met.

Ageing Hydro model sheets in LDPE bags, caused the bags to change both in appearance and texture (Figure 6.11). Bags became softer and crinkled. Samples adhered to LDPE bags and, on removal, droplets of DEHP (identified using FTIR spectroscopy) were observed on an area corresponding to that of model sheet on the inside surface. LDPE is known to be a good adsorbent for phthalate plasticizers (Sears and Darby, 1982).

Discolouration and tackiness of Solvay model sheets

All Solvay model sheets were water-white and transparent immediately after preparation and conditioning. However ageing in some environments caused sheets to develop a yellow or brown colouration either evenly over the whole sheet or in discrete areas. The differences between mean optical density for unaged sheets and the maximum optical density measured after 65 days in each environment were calculated, and are presented in Table 6.8. A change in optical density of one density unit may be detected with the naked eye.

When discolouration was unevenly distributed in a sample, the percentage of the discoloured area is included. In the table, environments are ranked in order of that having least effect on optical density of aged samples (first in table) to that having greatest effect (last in table). Total increase in optical density for all Solvay model sheets aged in a particular environment was calculated; the total was used to rank environments.

Some samples also became tacky, slightly sticky to the touch on ageing and this is denoted by ‘T’ in the table. Tackiness is not usually considered to be an optical property, however it influenced the appearance of sheets by adhering dust and particles from adsorbent materials used in the experimental environments, especially activated carbon.

Table 6.8 Change in appearance and tackiness of Solvay model sheets after ageing

<u>Key to table</u>
upper number -increase in optical density
middle number -percentage of sheet's area which is discoloured (unevenly discoloured samples only)
lower letter -'T' denotes sample had tacky surfaces

Increase in optical density after 65 days in ageing environment

environ-ment	Solvay 16.7%	Solvay 23.1%	Solvay 28.7%	Solvay 33.3%	Solvay 37.5%	Solvay 44.4%	Solvay 50%
closed	0	0	0	0 T	0 T	0 T	0 T
high RH	0	0	0	1	0	1	0
freezer	1	0	1	1 T	0 T	0 T	0 T
LDPE bag	2 T	1 T	1 T	0 T	0 T	0 T	0 T
open oven	2	2	1	0	0	0 T	0 T
Ageless oxygen absorber	0	2	5	3	2	1	1
open glass plate	18 2.2% T	7 15.7% T	1 45.0% T	3 4.2% T	3 T	2 T	0 T
activated carbon	27 94.7%	1 89.3%	5 89.4%	4 T	4 36.6% T	6 T	1 T
silica gel	5 9.9%	1 15.4%	30 30.6%	18 23.1%	22 65.4% T	18 15.1% T	4 T

In general, where discolouration occurred, Solvay sheets containing lower concentrations of DEHP exhibited greater increase in optical density than more highly plasticized samples. Ageing in a closed environment produced no increase in optical density, while ageing with silica gel (Figure 6.12) or activated carbon (Figure 6.14) produced unacceptable darkening of sheets, particularly for less plasticized sheets.

Ageing with silica gel produced a noteworthy phenomenon. During ageing, sheets were suspended vertically in the centre of flasks and directly above silica gel. Discolouration started at the lower edge of the sheet, that closest to the silica gel and, with time, progressed towards the upper edge. The rate of progression varied with different model sheets.

After 65 days, the discoloured area increased in the following order (percentage of area affected is recorded in Table 6.8):

Solvay 50.0% (smallest percentage area of discolouration)
Solvay 44.4%
Solvay 16.7%
Solvay 23.1%
Solvay 33.3%
Solvay 28.7%
Solvay 37.5% (greatest percentage area of discolouration)

The order did not correlate readily with sheet thickness, neither did it fit exactly with the rate or percentage of plasticizer lost from each sheet. One possible explanation was the movement of air and, therefore, also plasticizer vapour in the flask. Silica gel adsorbed plasticizer and water vapour from the atmosphere and the model sheet contained in the flasks. Model sheets lost plasticizer to the silica gel by diffusion. Since the silica gel was placed in the base of the flask, plasticizer vapour was pulled downwards together with air, agitating the air around the sheet. This uneven downwards agitation was likely to encourage plasticizer loss from the most available positions first, those closest to the adsorbent, and subsequently from positions further from the adsorbent. If this was the case, plasticizer loss was associated with discolouration of the model sheets.

Figure 6.12 Solvay model sheets before (upper sample) and after thermal ageing with silica gel. Discolouration is uneven and greatest at the lower edge of all sheets, that closest to the silica gel during ageing.
Left to right: Solvay 16.7%, 23.1%, 28.7%, 33.3%, 37.5% 44.4%, 50.0%

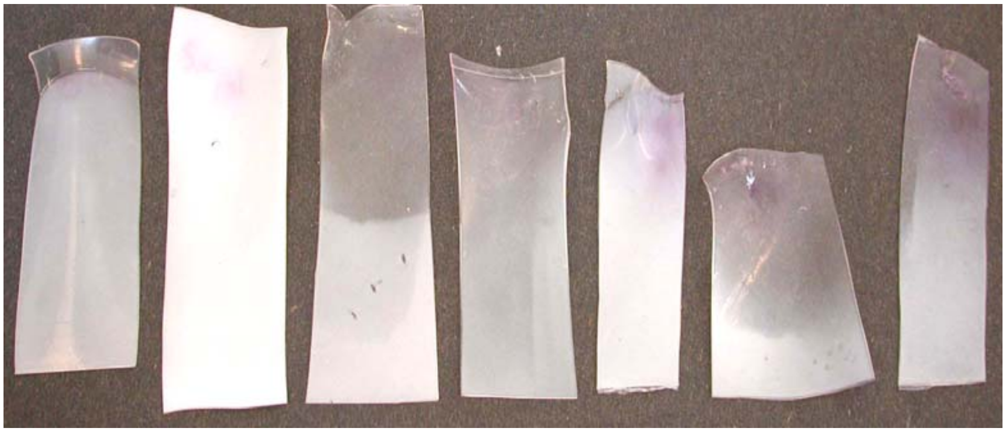


Figure 6.13 Solvay model sheets after ageing at high RH for 65 days. Left to right:
Solvay 16.7%, 23.1%, 28.7%, 33.3%, 37.5% 44.4%, 50.0%

Ageing in a high RH environment caused sheets to become appear cloudy or white and opaque (Figure 6.13). Discrete droplets of plasticizer were visible at the surface. However, after removing sheets from the environment and allowing them to dehydrate fully, very little change in the original optical density was visible. A similar phenomenon to that observed for sheets aged with silica gel was seen with samples aged in high RH. Opacity formed first at the lower edge of all sheets, that closest to the source of water and progressed towards the upper edge. After removal from the ageing environment, sheets containing higher levels of DEHP dehydrated more rapidly than less plasticized samples.

Ageing in LDPE bags resulted in softening and adsorption of DEHP by the bags as described for Hydro sheets previously.

Ageing on an open glass plate produced a pattern of brown patches on Solvay model sheets (Figures 6.15 and 6.16). Colourless areas corresponded to the presence of droplets of plasticizer between the surface of the sheet and that of the glass plate. The patches corresponded to dry, droplet-free areas. This suggested that the liquid plasticizer may have inhibited the discolouration due to dehydrochlorination of the PVC polymer.

Figure 6.14 Solvay model sheets before (upper sample) and after thermal ageing with activated carbon for 65 days. Sheets containing least plasticizer were most discoloured. Carbon particles adhered to the tacky surfaces of more highly plasticized sheets.
Lower row (left to right):
Solvay 16.7%, 23.1%, 28.7%, 33.3%, 37.5% , 44.4%, 50.0%

Figure 6.15 After ageing on open glass plates, brown patches formed on Solvay model sheets. Their location correlated well with the absence of plasticizer droplets trapped between the glass plate and the underside of the model sheet.

Upper row: unaged sheet
Lower row (left to right):
Solvay 16.7%, 23.1%, 28.7%, 33.3%, 37.5% , 44.4%, 50.0%

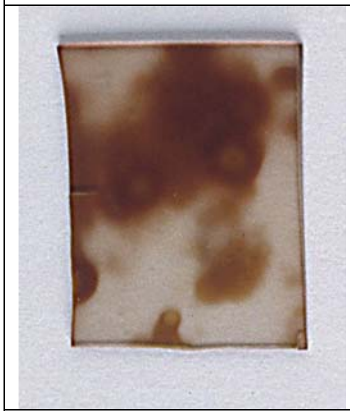


Figure 6.16 Closer image of Solvay 16.7% model sheet after thermal ageing on glass plate. This sheet was the most unevenly discoloured.
Sample dimensions: 20 x 15 x0.5mm.

Discolouration and tackiness of ‘objects’

Samples of microscope cover and tube were already slightly discoloured due to natural ageing prior to exposure to experimental environments. It was likely that most of the thermal and photo-stabilizers included at the formulation stage were now exhausted; this was the most likely cause of the increased discolouration compared with model sheets during ageing.

Ageing in some environments caused the optical density to increase as the colour darkened. The differences between mean optical density for unaged ‘objects’and the maximum optical density measured after 65 days in each environment were calculated, and are presented in Table 6.9. When discolouration was unevenly distributed in a sample, the percentage area discoloured is included. The presence of tackiness at the surfaces of films is also shown.

In the table, environments are ranked in order of that having least effect on optical density of aged samples (first in table) to that having greatest effect (last in table). Total increase in optical density for ‘objects’ aged in a particular environment was calculated; the total was used to rank environments.

Table 6.9 Change in appearance and tackiness of 'objects' after ageing

Key to table
upper number -increase in optical density
middle number -percentage of sheet's area which is discoloured (unevenly discoloured samples only)
lower letter -'T' denotes sample had tacky surfaces

Increase in optical density after 65 days in ageing environment

environment	**microscope cover**	**tube**
freezer	0 T	0 T
high RH	0 T	1 T
open glass plate	7 15.1% T	6 25.0% T
open oven	5 4.7% T	9 27.1% T
LDPE bag	4 20.2% T	11 19.8% T
closed	5 19.8% T	11 17.6% T
Ageless oxygen absorber	6 21.3% T	10 18.4% T
silica gel	12 23.0% T	15 26.4% T
activated carbon	14 19.2% T	17 56.0% T

Although changes in optical density of samples of tube were greater than those of the microscope cover, ageing environments had a similar effect on both 'objects'. The relatively high increases in optical density for the tube may be attributed to its greater thickness compared with that of the microscope cover; this could reduce the intensity of light transmitted. Ageing in a freezer caused no change in optical density and ageing with activated carbon caused the greatest increase in optical density for both objects. Discolouration was unevenly distributed in both 'objects' after ageing in most environments. Samples of microscope cover developed brown patches after ageing with silica gel, Ageless® oxygen absorber and activated carbon (Figure 6.17).

Figure 6.17
Microscope cover before (right) and after thermal ageing with activated carbon. Discolouration was uneven.
Sample dimensions: approximately 40x20x 0.5mm

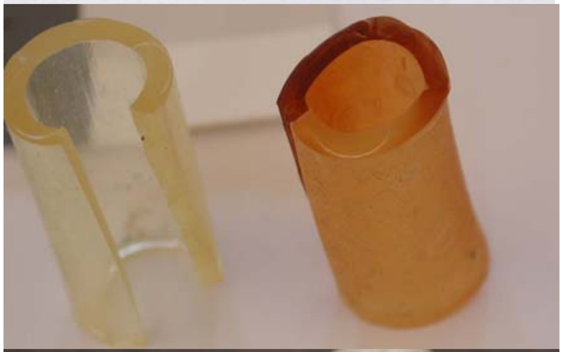


Figure 6.18
Tube before (left) and after accelerated thermal ageing with activated carbon. Note the uneven discolouration of the aged sample. The darker half was closest to the carbon during ageing.
Sample dimensions: 1.5mm diameter x30mm

Figure 6.19
Tube before (left) and after thermal ageing at high RH for 65 days. The achieved opacity was reversed on dehydrating under ambient conditions.
Sample dimensions: 1.5mm diameter x 30mm

Samples of tube were aged horizontally and, particularly during ageing with activated carbon, one side which had been parallel to the base of the flask and, thereby, to the adsorbent material, became considerably darker than the upper side which ‘faced’ the cap (Figure 6.18). It appeared as if more plasticizer had been adsorbed from the lower edge, promoting discolouration in that localized area.

Ageing at high RH caused ‘objects’ to appear white. The opacity highlighted the appearance of adhered dust and hairs on the tacky exterior surfaces of both microscope and tube (Figure 6.19). Just as for model sheets, after ‘objects’ were removed from the environment and allowed to dehydrate, little change in the original optical density was visible. The microscope cover required 8 hours to fully regain its original transparency while the tube required 26 hours. The difference in the period required was probably due to the greater thickness of the tube (2mm) compared with the microscope cover (0.5mm).

Low Vacuum- Scanning electron microscopy (LV-SEM)

Model sheets and ‘objects’ were examined for changes in morphology before and after ageing. Unmounted cross-sections were also mapped for distribution of elemental carbon, oxygen and chlorine. The areas with the brightest or lightest appearance on maps were those containing the highest concentration of that element being analysed. Chlorine was associated only with PVC and not with plasticizer, while oxygen was used as an indicator for DEHP and Eastman TXIB (present only in Solvay formulations).

Oxygen would also be an indicator for the presence of some degradation products of DEHP, including crystalline phthalic anhydride or acid. Samples aged in environments containing activated carbon did not produce useful images or maps since small particles of carbon were always present on their surfaces.

LV-SEM of Hydro model sheets

LV-SEM examination of Hydro model sheets suggested the bulk of sheets to have a homogeneous morphology. Mapping for oxygen and chlorine identified DEHP evenly distributed throughout the bulk. No pinholes were identified in the sheets at higher magnification (x 750), in contrast to Solvay samples. All unaged Hydro model sheets had distinct thin layers at upper and lower surfaces, increasing in thickness from 0.01mm for Hydro 33.3% and 37.5% to 0.02mm for Hydro 44.4% and 0.03mm for Hydro 50%. Mapping suggested that the layers contained higher levels of oxygen than the bulk of the film, but had reduced levels of chlorine. Distinct thin layers contained more plasticizer than other areas in the model sheet. The presence of chlorine, indicated that the layer was not pure plasticizer, but was enriched in plasticizer compared with the bulk composition.

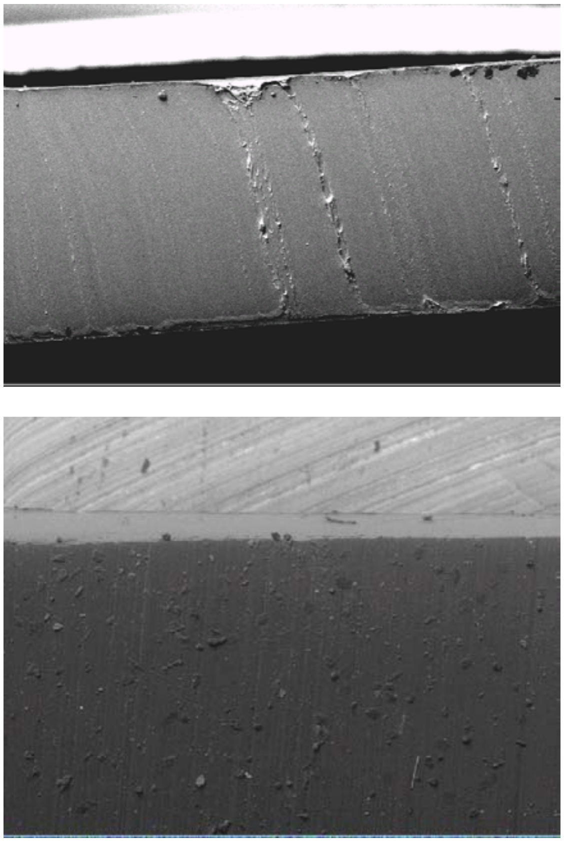


Figure 6.20
Scanning electron micrograph (secondary electrons) of Hydro 33.3% model sheet. Cross-section of model sheet before ageing. Distinct thin layer of plasticizer (0.01mm) is visible at upper surface.

Examining the upper surface from above, droplets of plasticizer are evident as dark spots, suggesting that the layer is 'real' and not an artefact of the technique used. Elemental mapping showed that the droplets contained oxygen, indicative of DEHP.

The possibility that the appearance of the distinct thin layers may have been an artefact due to the geometry of the detector in relation to the sample in the LV-SEM, was investigated by imaging and mapping the upper surface of the sheet, at right angles to the cross-section. In every case, it also contained a higher concentration of oxygen than the bulk, suggesting that the phenomenon was real (Figure 6.20).

By contrast to Solvay model sheets, distinct thin layers remained at the surfaces of all Hydro model sheets after ageing in all environments for 65 days, with the exception of those enclosed in LDPE bags. On removing model sheets from LDPE bags, droplets were observed on the inside surface of the enclosure; they were subsequently identified as DEHP by ATR-FTIR spectroscopy.

The difference in morphology between Solvay and Hydro model sheets on ageing, indicated that the additional presence of Eastman TXIB co-plasticizer promoted migration and loss of DEHP from the surface of Solvay model sheets. Eastman TXIB was more volatile than DEHP, so was likely to migrate and evaporate from surfaces more rapidly. It may have acted as a carrier solvent to transport DEHP to the surface. When DEHP was the sole plasticizer, as in Hydro model sheets, migration and loss of plasticizer from the surfaces appeared minimal.

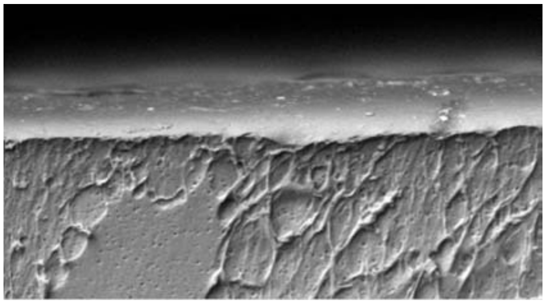


Figure 6.21 SEM of cross-section of unaged model sheet of Solvay 50.0%. Note distinct thin layer at surface. Sample is 0.25mm high

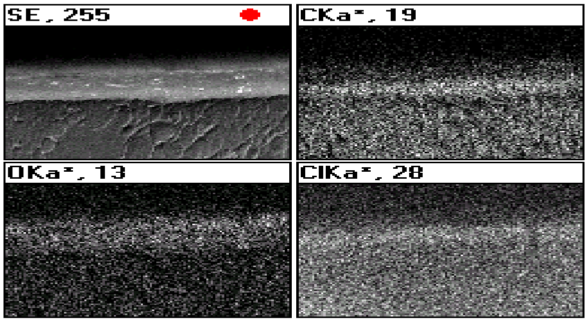


Figure 6.22 Elemental mapping by SEM of unaged Solvay 50.0% model sheet. Clockwise from top left-image-mapping of carbon-mapping of chlorine (in PVC)-mapping of oxygen (in plasticizer)

LV-SEM of Solvay model sheets

Scanning electron micrographs of cross-sections of unaged Solvay 16.7%, 23.1 and 28.6% model sheets, showed homogeneous material, often with a few inclusions near surfaces. Mapping for oxygen showed that these inclusions contained higher oxygen than the surrounding film while mapping for chlorine suggested that they were depleted in that element. Since oxygen was only associated with DEHP and Eastman TXIB components in the Solvay formulation, and not with PVC, it was concluded that they were droplets of plasticizer. Examination at higher magnification (x 750) revealed pinholes in the bulk of the sheets. They may have been formed as plasticizer migrated towards the heated surfaces of the press during processing (Figures 6.21 and 6.22).

Scanning electron images of cross-sections of Solvay 33.3%, 37.5%, 44.4% and 50.0% model sheets prior to ageing, showed the presence of distinct thin layers at upper and lower surfaces. Mapping suggested that the layers contained higher levels of oxygen than the bulk of the film, but had reduced levels of chlorine. Distinct thin layers contained more plasticizer than other areas in the model sheet. The presence of chlorine, albeit in reduced concentrations compared with the bulk, indicated that the layer was not pure plasticizer, but was enriched in plasticizer compared with the bulk composition.

As when examining Hydro model sheets, the possibility that the appearance of these layers may have been an artefact due to the geometry of the detector in relation to the sample in the LV-SEM, was investigated by mapping the upper surface of the sheet, at right angles to the cross-section. In every case, it also contained a higher concentration of oxygen than the bulk, suggesting that the phenomenon was real. Since no crystalline materials were observed by LV-SEM on any model sheet before or after ageing, it was most likely that the elemental oxygen originated from plasticizer and not degradation products. Model sheets had not been aged , indicating that plasticizer was present at the surfaces of sheets containing 33.3% DEHP and higher levels immediately after preparation.

Ageing in a freezer had no effect on the morphology of Solvay model sheets (Table 6.10). Ageing in open oven, on open glass plates, in LDPE bags, with silica gel and at high RH resulted in the presence of plasticizer droplets at surfaces for all Solvay model sheets. This suggested that Solvay model sheets which contained 33.3% or more DEHP, had their original plasticizer layers reduced to droplets by the ageing process. Although samples aged in LDPE bags did not have layers of plasticizer at their surfaces, droplets of plasticizer were identified on the inside surfaces of bags, suggesting that the LDPE had adsorbed plasticizer from the Solvay model sheets.

Ageing in a closed environment promoted the formation of distinct thin layers in Solvay 16.7%, 23.1% and 28.7% model sheets. However, they did not feel tacky, probably because the layers were so thin. It seems likely that the above ambient temperature promoted migration of plasticizer to the surface, but the closed environment inhibited the extent and rate of evaporation of plasticizer from the surface before equilibrium conditions were achieved.

Table 6.10 Presence of separate plasticizer layer and plasticizer droplets from LV-SEM examination of Solvay model sheets

environ-ment	**Solvay 16.7%**	**Solvay 23.1%**	**Solvay 28.7%**	**Solvay 33.3%**	**Solvay 37.5%**	**Solvay 44.4%**	**Solvay 50%**
unaged	no layer	no layer	no layer	layer 0.02mm	layer 0.01mm	layer 0.02mm	layer 0.02mm and droplets
closed	layers 0.01mm	layers 0.01mm	layers 0.01mm	layers 0.02mm	layers 0.02mm	layers 0.02mm	layer 0.02mm
freezer	no layer	no layer	no layer	no layer	layer 0.01 mm	layer 0.02mm	layer 0.02mm
high RH	no layer droplets	no layer droplets	no layer droplets	no layer droplets	no layer droplets	no layer droplets	no layer droplets
silica gel	no layer droplets on surface	no layer droplets on surface	no layer droplets on surface	no layer droplets on surface	no layer droplets on surface	no layer droplets on surface	no layer droplets on surface
Ageless oxygen absorber	no layer	no layer droplets	no layer droplets	no layer droplets	layer 0.01mm and droplets	layer 0.02mm	layer 0.02mm
open oven	no layer	no layer droplets	no layer droplets	no layer droplets	no layer droplets	no layer droplets	no layer droplets
open glass plate	no layer droplets on contact surface	no layer droplets on contact surface	no layer droplets on contact surface	no layer droplets on contact surface	no layer droplets on contact surface	no layer droplets on contact surface	no layer droplets on contact surface
LDPE bags	no layer	no layer	no layer	no layer	no layer	no layer	no layer

LV-SEM of 'objects'

Samples of microscope cover and tube were examined before and after exposure to experimental environments. Cross-sections of microscope cover showed the presence of many small holes, with various diameters, which imparted an inhomogeneous, sponge-like appearance to the structure (Figure 6.23). A thin layer of plasticizer was identified on one surface, varying in thickness from 0.01 to 0.02mm, though this was dependent on location.

Ageing in a freezer (Figure 6.24), in a LDPE bag, at high RH and with Ageless® oxygen absorber were the only environments to change the morphology of the microscope cover. After 65 days in these environments, additional large polyhedral or spherical, droplets had accumulated within the bulk and near the surfaces of the 'object'. They were identified as plasticizer using elemental mapping as previously described.

Sections of tube were examined end-on and seen to have a homogeneous structure prior to ageing in experimental environments. Distinct layers of DEHP was identified on outside (0.03mm thick) and inside (0.01mm thick) surfaces of the tube. No difference in distribution of plasticizer was observed after ageing in any environment, with the exception of LDPE bags. Samples aged in bags formed large groups of plasticizer droplets in the bulk and at the outside surface of the tube.

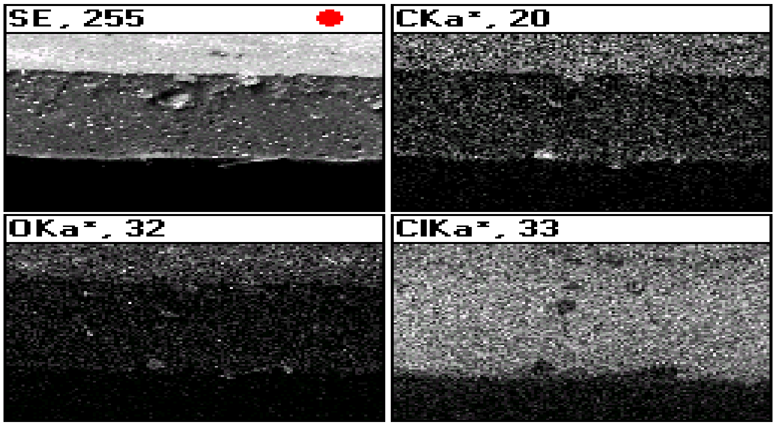


Figure 6.23
Above: From top left, clockwise-SEM image of cross section of microscope cover before accelerated ageing, map for elemental carbon, map for elemental chlorine, showing that film has a high concentration of that element and (lower left) map for elemental oxygen, brighter areas indicating enrichment of DEHP at surface.

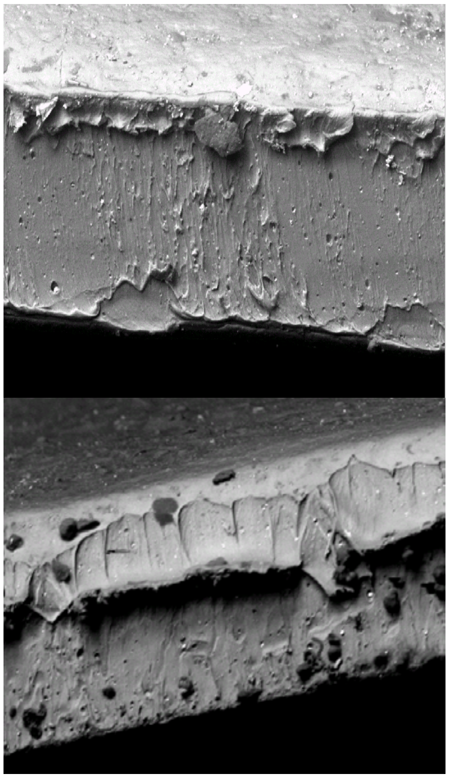


Figure 6.24
Upper: SEM secondary image of cross section through microscope cover (0.5mm thick) before accelerated ageing.

Lower: SEM secondary image of cross section through microscope cover after ageing in a freezer for 65 days and returned to ambient conditions. Plasticizer droplets (dark spots) have accumulated at upper and lower surfaces.

Discussion of LV-SEM results

In conclusion, all model films formulated with 33.3% and higher concentrations of DEHP, already had distinct thin layers at their surfaces before ageing. These layers were enriched in plasticizer compared with the bulk composition. Formulations containing less than 33.3% DEHP were homogeneous in composition, with no additional layers. Objects also had layers of plasticizer at their surfaces prior to ageing.

Ageing in a freezer caused no change to the morphology of model sheets, but promoted migration of plasticizer droplets in the microscope cover. This may indicate reduced compatability between DEHP and degraded PVC at low temperatures compared with undegraded PVC found in model sheets. However, it was not possible to further investigate this phenomenon within the scope of the project.

Ageing in closed environments promoted the formation of distinct thin layers in model sheets formulated with less than 33.3% DEHP. It was likely that plasticizer had evaporated from the surface of the sample aged at 70°C and when the concentration in the airspace close to the sheet surface had attained the same plasticizer concentration as that close to the surface, no further plasticizer had been lost. However, plasticizer had diffused from the bulk of the film to replace that lost from the surface and it formed a distinct thin layer.

As discussed in the previous section concerning LV-SEM of Hydro model sheets, the differences in behaviour between Solvay and Hydro model sheets on ageing may be attributed to the presence of Eastman TXIB co-plasticizer in the Solvay formulations. The co-plasticizer may act as a carrier solvent which transported DEHP to the surface more rapidly than when DEHP was present alone .

Summary of results of all analytical techniques

Findings from all analytical techniques indicated that the environment in which model sheets and objects were aged, influenced the extent of plasticizer loss, the rate and mechanism by which it was lost. Model sheets and objects containing similar levels of plasticizer behaved in a similar way in the same environment, irrespective of their different histories. Despite the advanced state of degradation exhibited by some samples, namely the microscope cover and tube, the rate of further degradation could be slowed or accelerated by storage environment. Relating this observation to conservation practice, indicates that passive conservation of plasticized PVC is likely to be effective to some degree whatever the level of degradation of the object.

Enclosing samples of PVC with unstirred air was the most effective storage environment to retain plasticizer. Removal of oxygen or adsorption of volatiles from the storage environment was not as effective at inhibiting plasticizer loss as enclosing or lowering storage temperature. Storage of samples in lightly stirred air further increased the extent and rate of loss of plasticizer. However, placing samples in contact with a highly adsorbent material caused the greatest plasticizer loss.

This is rather contra-intuitive. Museum conservators and designers are usually advised either to improve ventilation or to include adsorbent materials to remove volatile degradation products from the air space surrounding plastics objects during storage. The results obtained in this research , suggest that such actions would accelerate the loss of plasticizer and reduce the longevity of both new and deteriorated PVC objects.

Rate and mechanism by which plasticizer was lost were not directly related to sample thickness or surface area of sample, but greatly influenced by storage environment. Weight loss and ATR-FTIR spectroscopy results indicated that plasticizer was lost at a rate controlled by diffusion from the bulk to surfaces when stored in lightly stirred air or in contact with a highly adsorbent material. In all other environments, the rate of loss was evaporation-controlled.

ATR-FTIR confirmed that ageing in closed environments and in the presence of adsorbents enabled samples to retain their original surface concentration of DEHP.

Ageing in lightly stirred air (open and open glass plate) and in contact with highly adsorbent material (LDPE bag) significantly reduced the surface concentration of DEHP. Loss of plasticizer caused by storing in these environments was likely to have occurred via a diffusion-controlled process since DEHP was lost too rapidly from the surfaces for it to be replaced immediately by diffusion from the bulk of the material. ATR-FTIR and headspace analysis also suggested that the ageing conditions investigated here were not sufficiently severe to degrade DEHP, only to mobilise and evaporate it.

Weight loss measurements and ATR-FTIR spectroscopy indicated that the presence of co-plasticizer Eastman TXIB in Solvay formulations, accelerated migration and loss of DEHP from the surfaces of model sheets, compared with the Hydro model sheets which contained DEHP alone. DEHP is considered a semi-volatile plasticizer while Eastman TXIB is classed as volatile (Wilson, 1995). Since TXIB and DEHP are highly compatible, it is likely that the former material transported the latter to the surface. From there, Eastman TXIB evaporated and deposited the less volatile DEHP.

Discolouration was influenced by environment for all model sheets and objects, but its magnitude was not solely related to plasticizer loss. The presence of droplets or a layer of plasticizer on the surface seemed to act as a protective surface coating to inhibit dehydrochlorination, the cause of darkening. This possibility was clearly illustrated by Solvay 16.7% model sheets aged on open glass plates. The transparent, clear areas between the dark brown spots showed good correlation with the location of DEHP droplets. In general, the tacky model sheets, those containing higher levels of plasticizer discoloured far less than those with non-tacky surfaces.

Addition of phthalate plasticizers to PVC has been shown to reduce the rate of dehydrochlorination by the polymer, by inhibiting the growth of polyene sequences. Ester groups in DEHP are thought to solvate the labile groups of the polymer chain which are responsible for the instability, thus avoiding double bond formation (Beltran and Marcilla, 1997). The inhibitive properties of DEHP are usually considered in terms of compounded PVC. However, since plasticizers are only physically mixed and then weakly physically bonded during fusion, it could be argued here that they still function as inhibitors if simply placed in close contact with degrading PVC.

This principle has been applied to other acid-producing plastics. The destructive denitration reaction of a cellulose nitrate mirror back dating from the 1920s was inhibited by immersing it in epoxidized soya bean oil (ESBO), also a plasticizer for PVC. ESBO was thought to adsorb the acidic nitric and sulphur oxides from the cellulose nitrate and thereby prevent them causing autocatalytic degradation (Morgan, 1993).

This theory was difficult to apply to the microscope cover and tube which were already tacky and degraded before the start of accelerated ageing. It seemed that despite reducing plasticizer loss from degraded objects using those storage methods applied to for model sheets, degradation of the PVC polymer continued nevertheless. This phenomenon was illustrated by the increases in optical density for microscope cover and tube. Microscope cover and tube were the only samples from which hydrogen chloride was detected, another strong indication of dehydrochlorination.

It seemed that the inhibitive properties of DEHP were less effective for PVC at an advanced state of deterioration. It is also known that compatibility between DEHP and PVC changes with deterioration of one or both of the components (Sears and Darby, 1982). The detection by LV-SEM of layers of plasticizer at the surfaces of model objects and the formation of large droplets of DEHP in the bulk after ageing in some accelerated ageing environments may indicate reduced compatibility between plasticizer and highly degraded PVC.

7. Conclusions

The three goals stated at the beginning of this thesis have been achieved. By examining and analysing deteriorated objects containing plasticized PVC, the major mechanism by which such objects deteriorate in museum storage collections was determined. Plasticizer was found to migrate from the bulk of the PVC to the surfaces of objects with time, manifested by increased tackiness of the surface. From there it either evaporated slowly or broke down by hydrolytic or oxidation mechanisms. Crystalline phthalic acid was the main degradation product identified at the surfaces of objects.

The PVC polymer component also degraded to form conjugated polyene systems of increasing length which discoloured the objects. Based on this examination, the useful lifetime of PVC objects was found to range from 10-35 years.

A non-destructive analytical technique was developed to quantify the concentration of di-2-ethylhexyl phthalate (DEHP) the most commonly identified plasticizer in museum objects containing PVC, at the surfaces of objects. Attenuated Total Reflection Fourier Transform infrared (ATR-FTIR) spectroscopy was established as a sufficiently sensitive technique to monitor the loss of DEHP from surfaces of objects and to identify the mechanism by which it was lost. The technique developed was also suitable for quantifying DEHP as one component in a plasticizer blend. Non-destructive low-vacuum scanning electron microscopy (LV-SEM) was used to map the distribution of DEHP and identified phase separation between DEHP and PVC where it occurred.

Model PVC formulations were developed to represent the range of plasticized PVC objects identified in museum collections. They underwent accelerated thermal ageing in environments, typical of those used to store and display plastics and other materials in museums. The rates of deterioration of model sheets were compared using the non-destructive techniques developed for the project.

Results suggested that the useful lifetime of plasticized PVC and the migration of plasticisers were related. DEHP inhibited the degradation of the PVC polymer, therefore when it was lost, PVC became discoloured and brittle. Degradation was inhibited from both model formulations and naturally degraded objects by enclosure in a non-adsorbent material such as glass, containing non-agitated air. Freezing also sucessfully minimised loss of plasticizer, but was less effective when the PVC component exhibited advanced deterioration. Storage on open environments such as glass shelf or wrapping objects in an adsorbent material such as polyethylene resulted in high losses of plasticizer.

Calculations based on the weight lost by model sheets during accelerated thermal ageing, and the rule of thumb concerning the rate of reactions with temperature, clearly indicated that the useful lifetime of plasticized PVC objects may be prolonged more than 10 fold at ambient conditions, by changing the storage environment from a polyethylene bag to a closed glass container or by placing the object in a freezer. Enclosing plasticized PVC objects, whatever their level of deterioration, is inexpensive to implement, of low practical complexity and allows public accessibility to plastics objects.

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Note: All references to Web sites are as found September 2001

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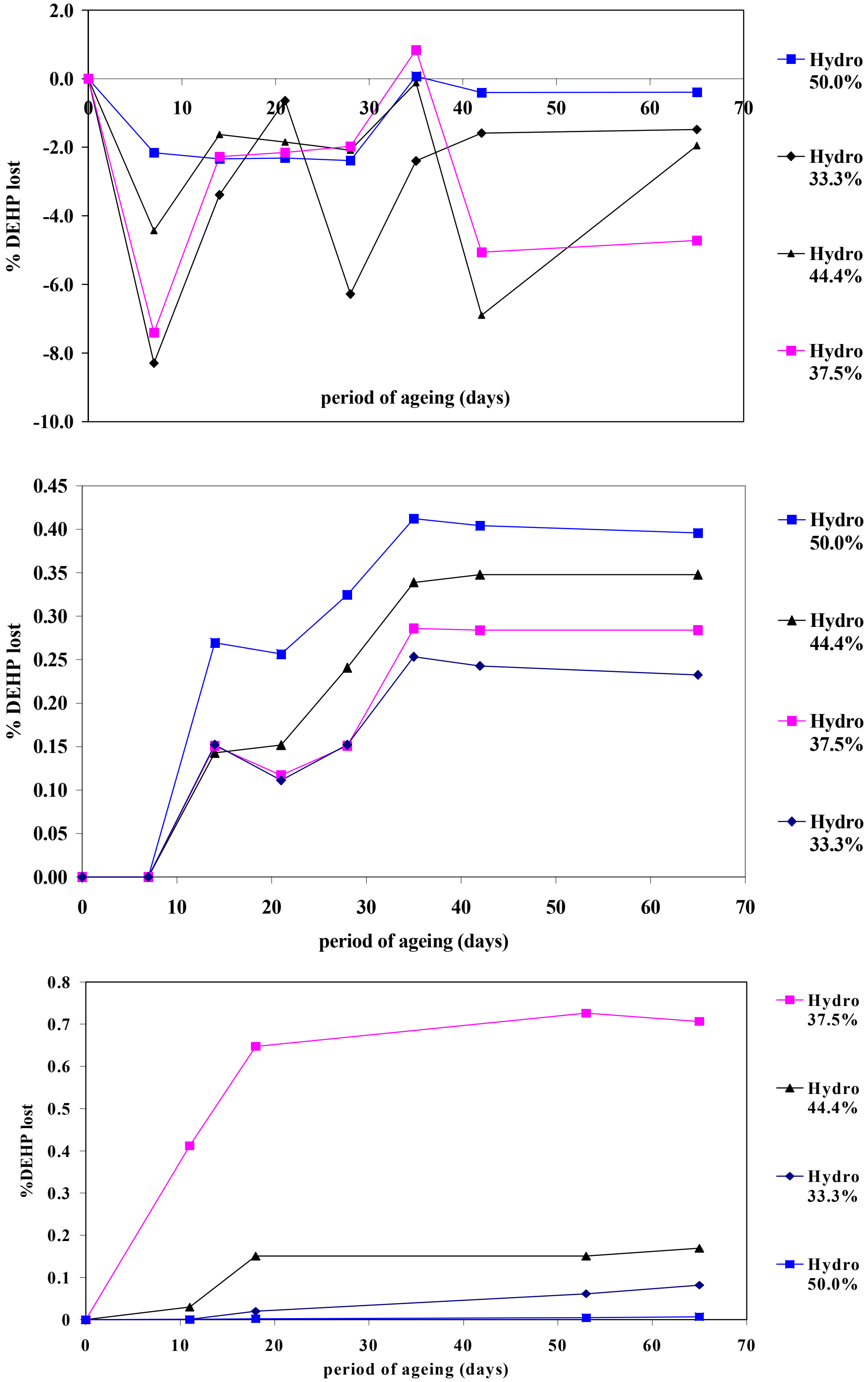
Appendices

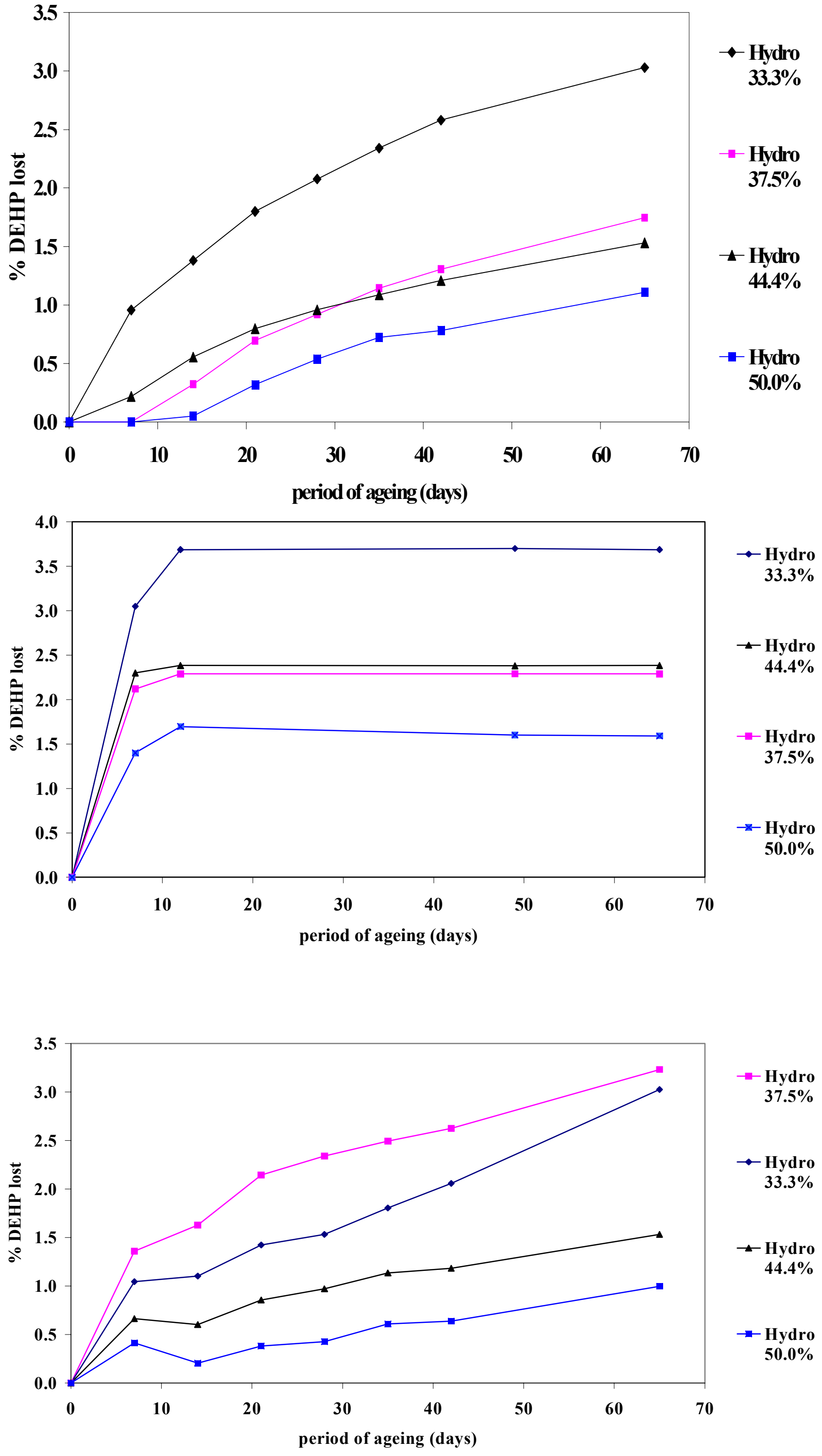
Appendix A- Results of weight loss measurements
Appendix A1-Results of weight loss measurements for Hydro model sheets
Appendix A2-Results of weight loss measurements for Solvay model sheets
Appendix A3-Results of weight loss measurements for ‘objects’

Appendix B- Results of FTIR spectroscopy
Appendix B1- Results of FTIR spectroscopy for Hydro model sheets
Appendix B2- Results of FTIR spectroscopy for Solvay model sheets

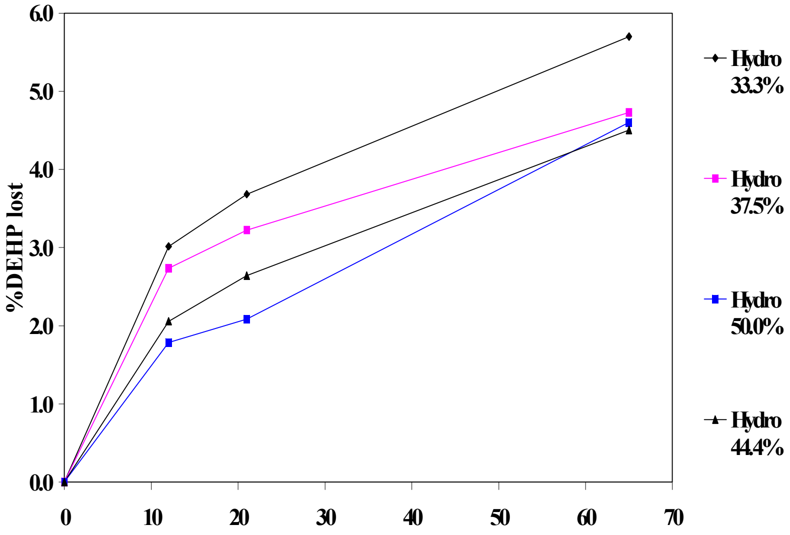
Appendix C-Suppliers of chemicals used

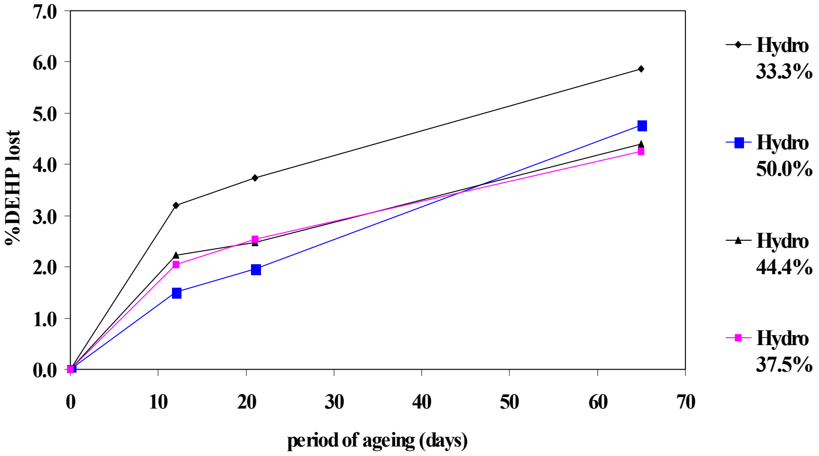


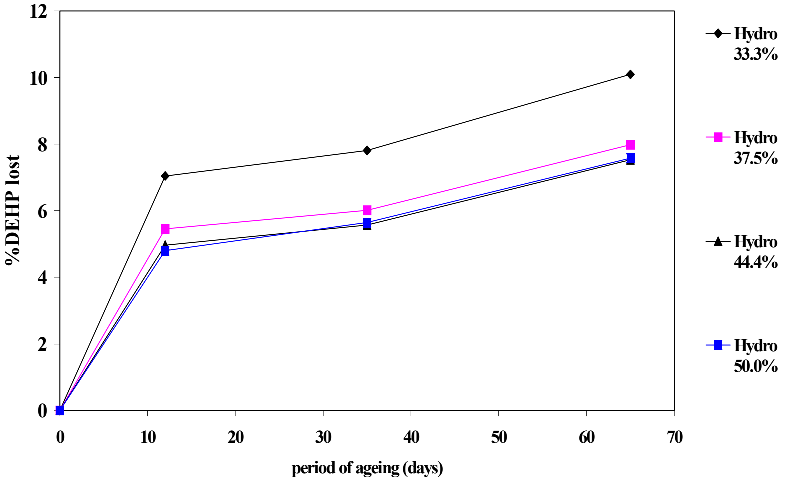
Percentage DEHP lost by Hydro model sheets aged at high RH (upper) in freezer (middle) and closed environments (lower)



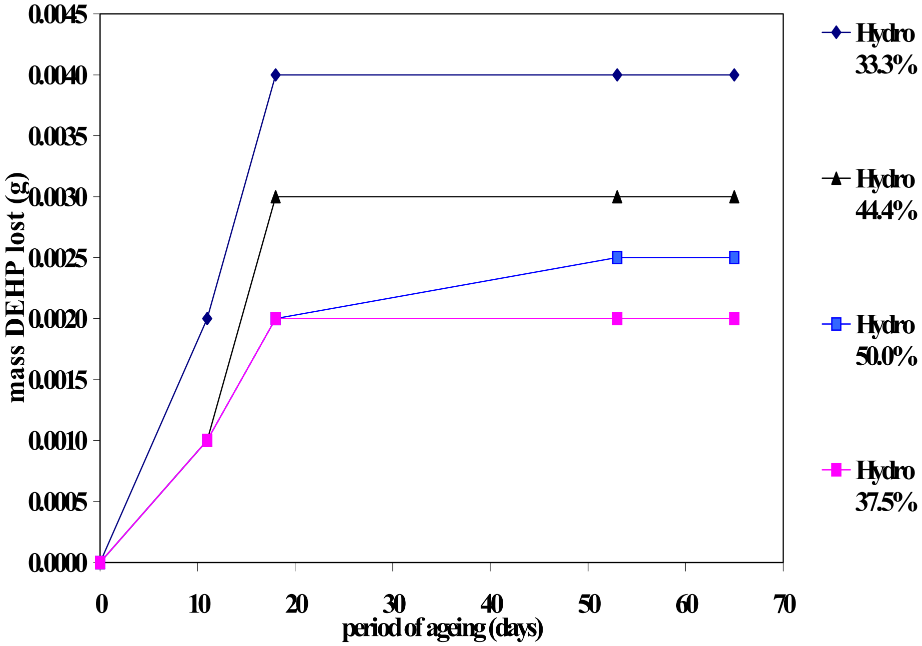
Percentage DEHP lost by Hydro model sheets aged with Ageless oxygen absorber (upper) with silica gel (middle) and with activated carbon (lower)

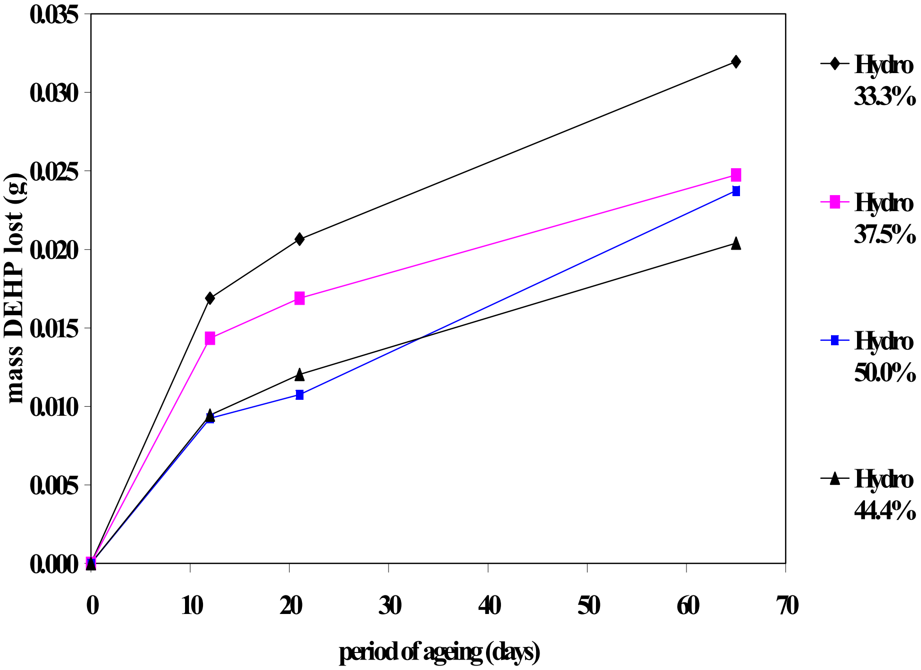




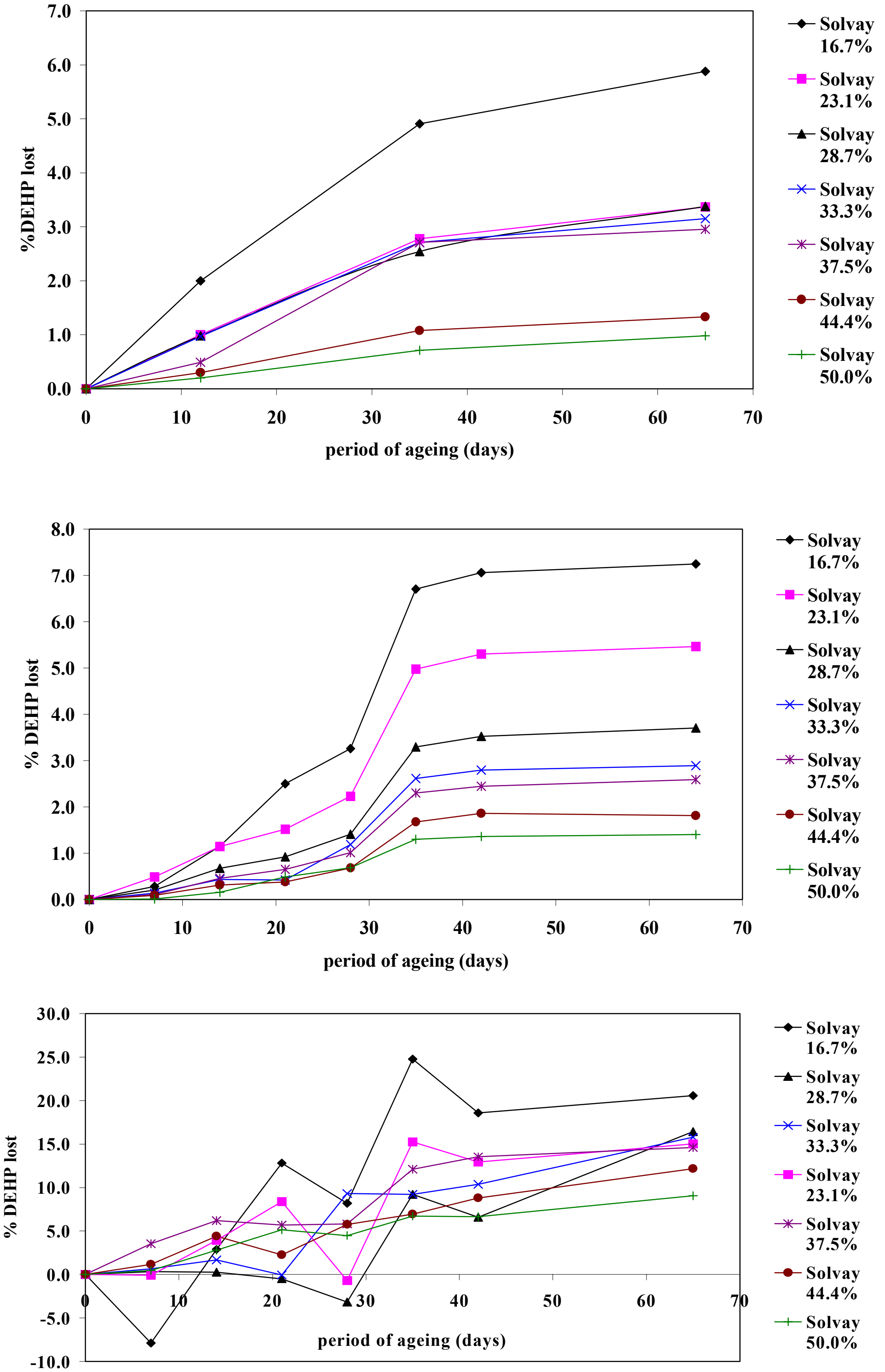


Percentage DEHP lost by Hydro model sheets aged in open oven (upper)on open glass plates (middle) and in LDPE bags (lower)

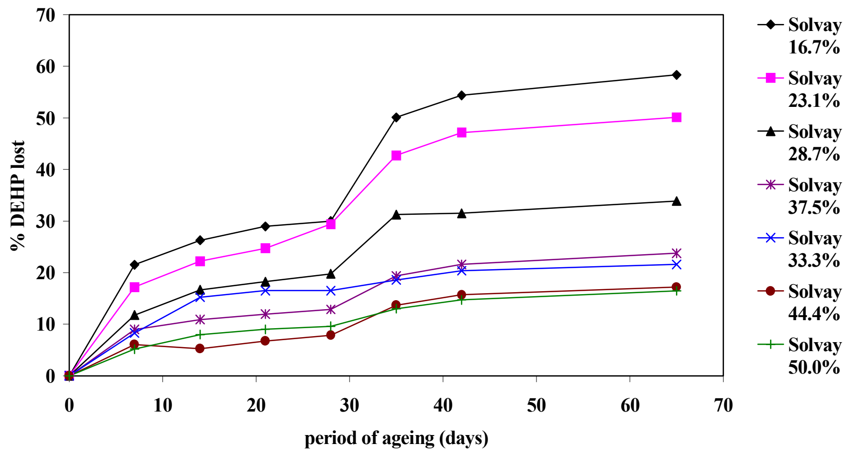


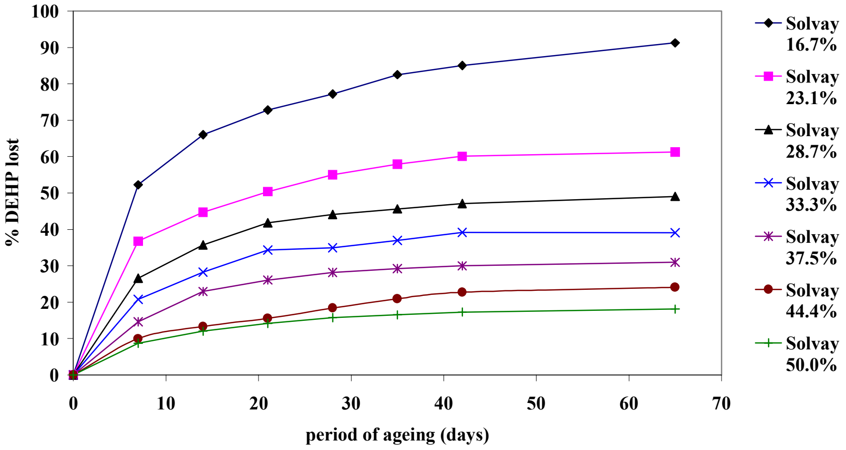


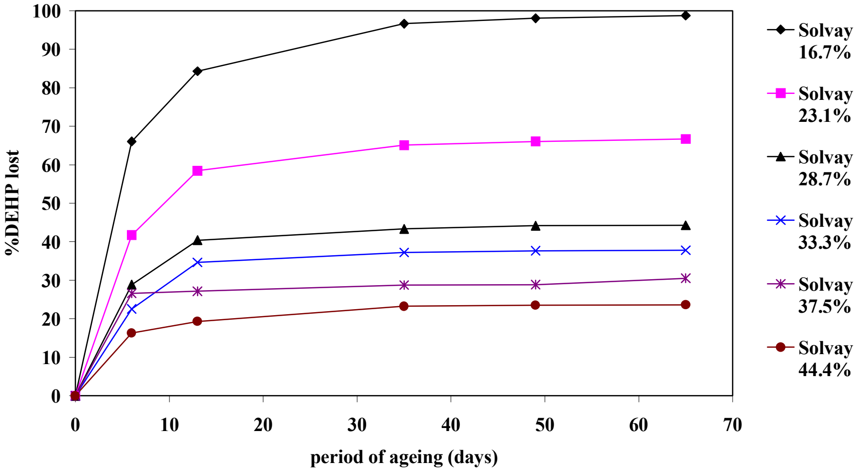
Comparison of mass DEHP lost from Hydro model sheets during accelerated thermal ageing in closed environments (upper) and in open oven (lower)



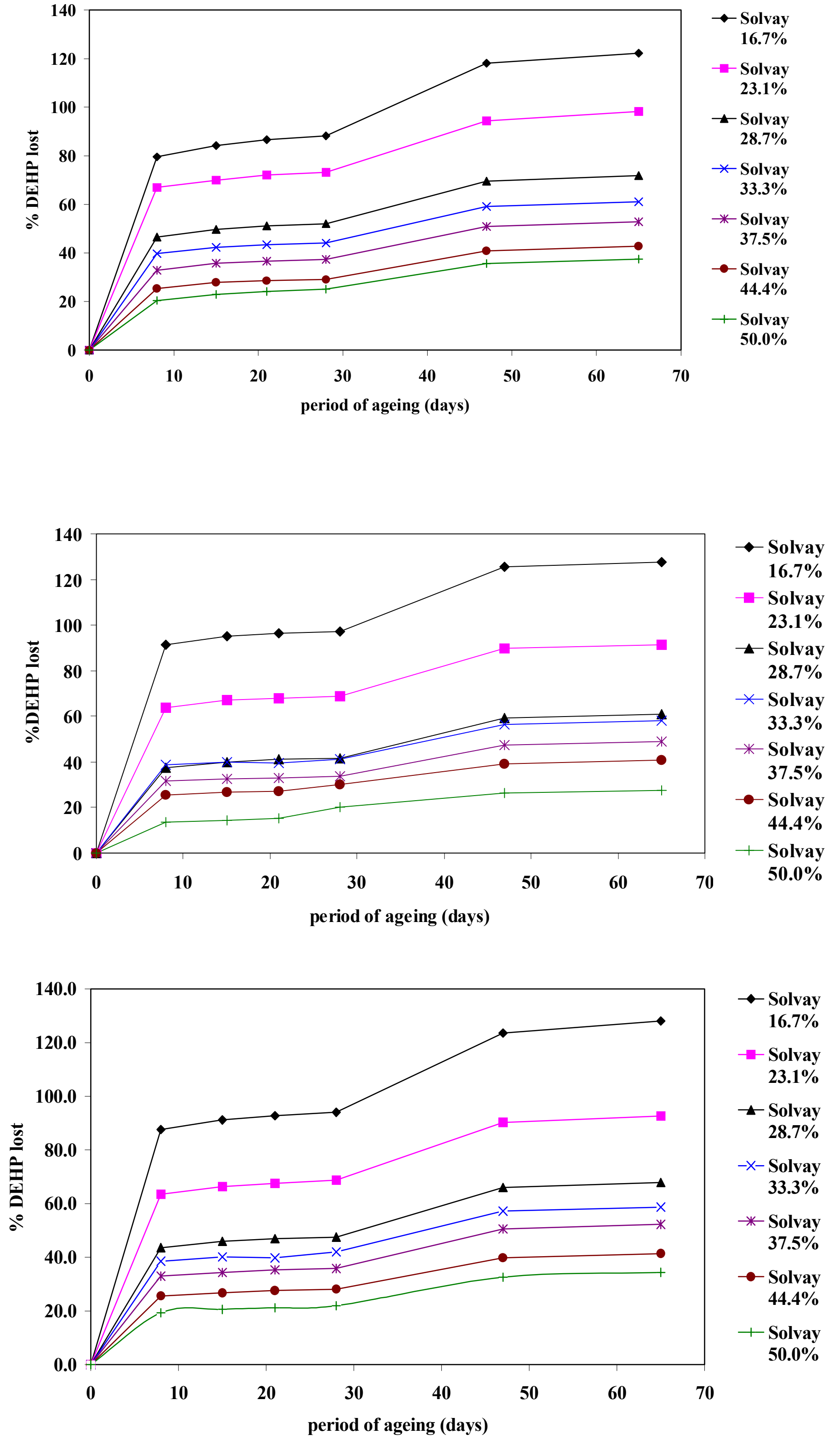
Percentage DEHP lost by Solvay model sheets aged in closed (upper) freezer (middle) and at high RH (lower)



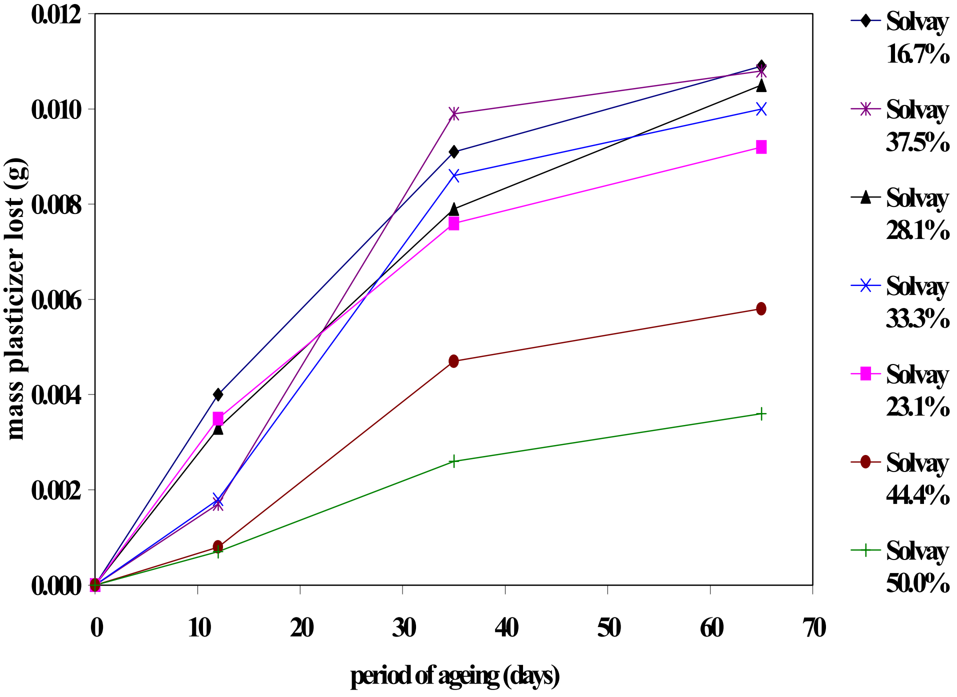


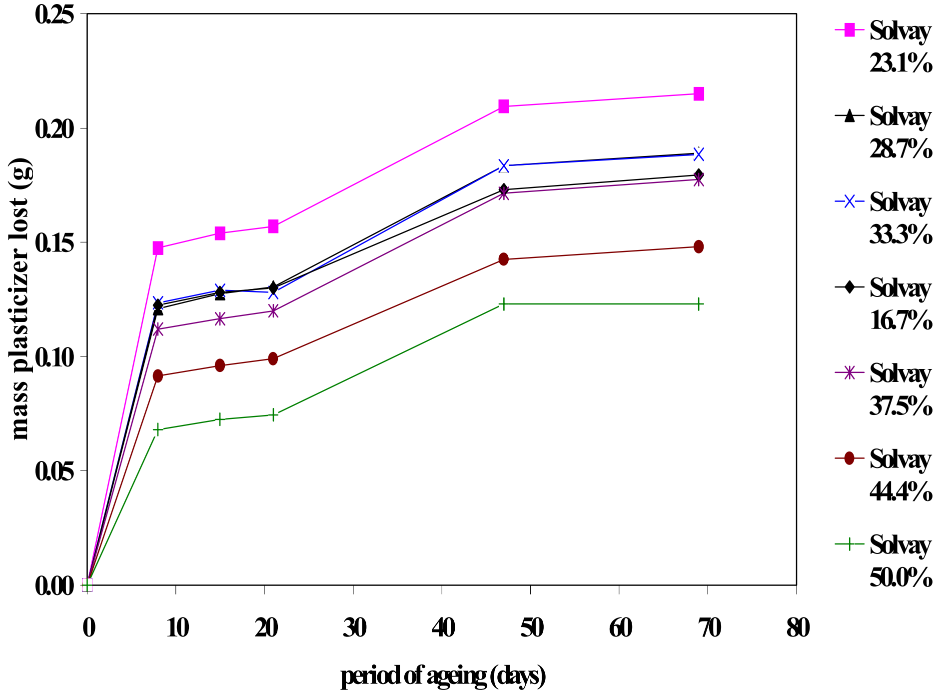


Percentage DEHP lost by Solvay model sheets aged with Ageless oxygen absorber (upper) with silica gel (middle) and with activated carbon (lower)

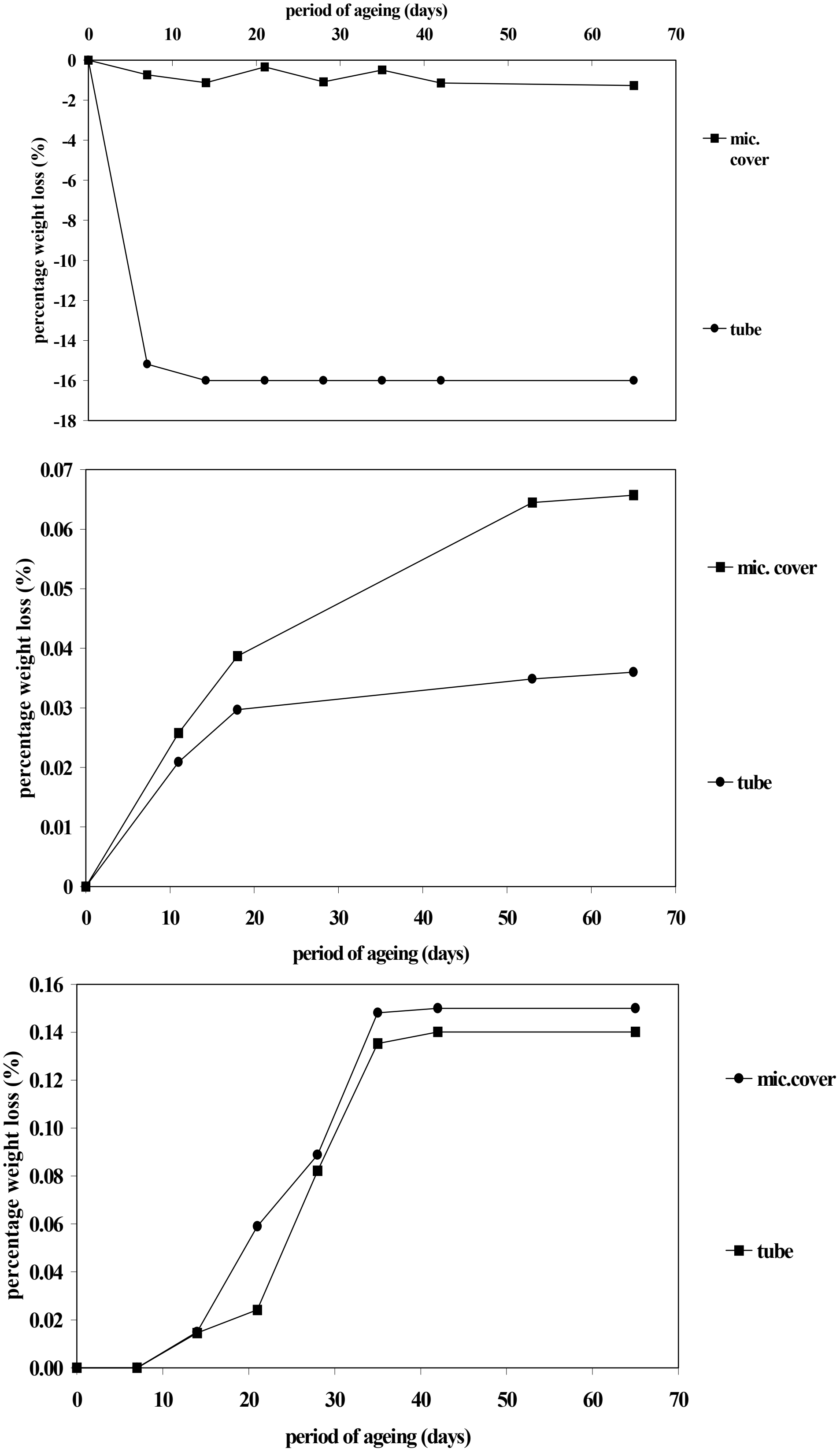


Percentage DEHP lost by Solvay model sheets aged in LDPE bags (upper) on open glass plate (middle) and in open oven (lower)

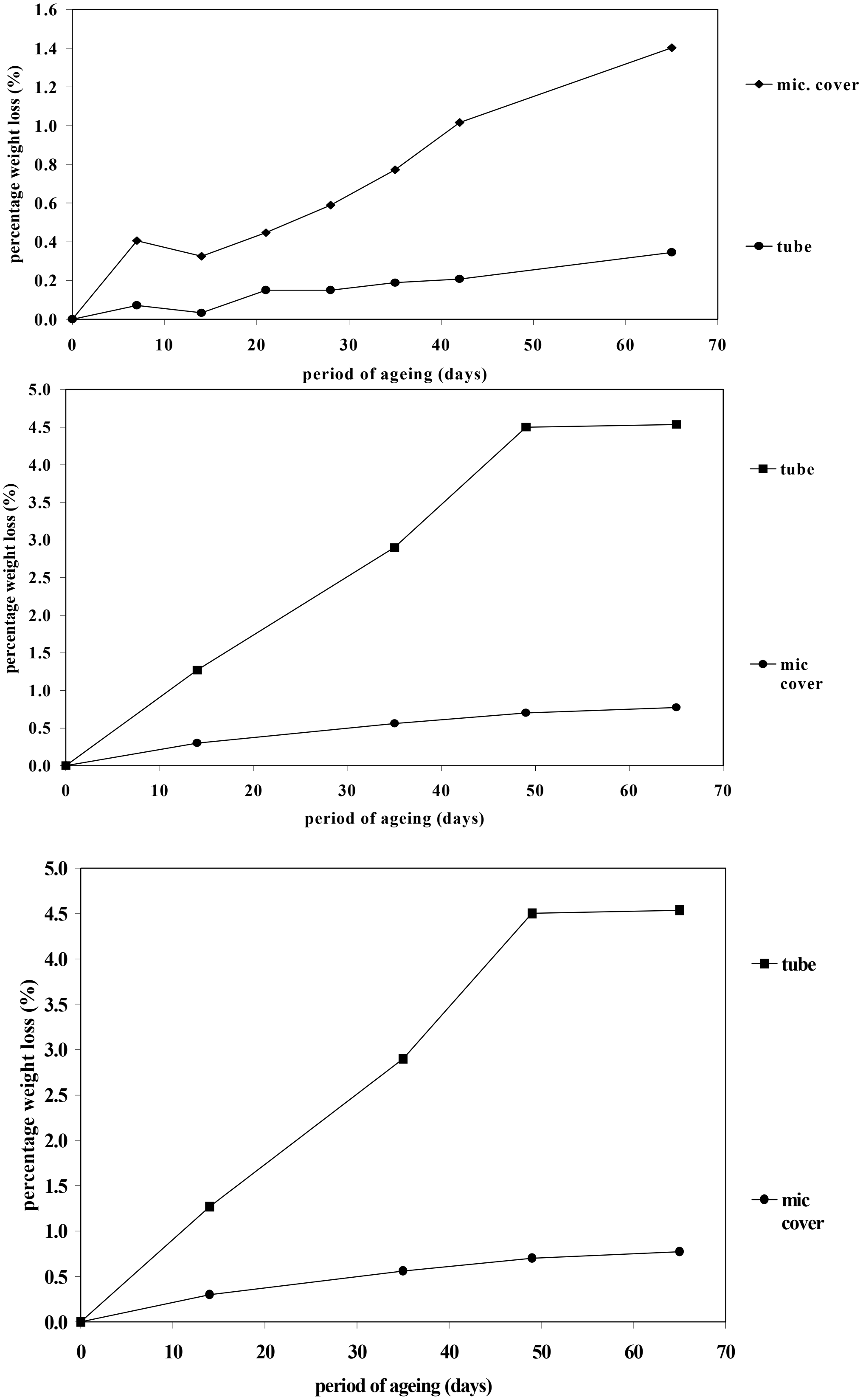




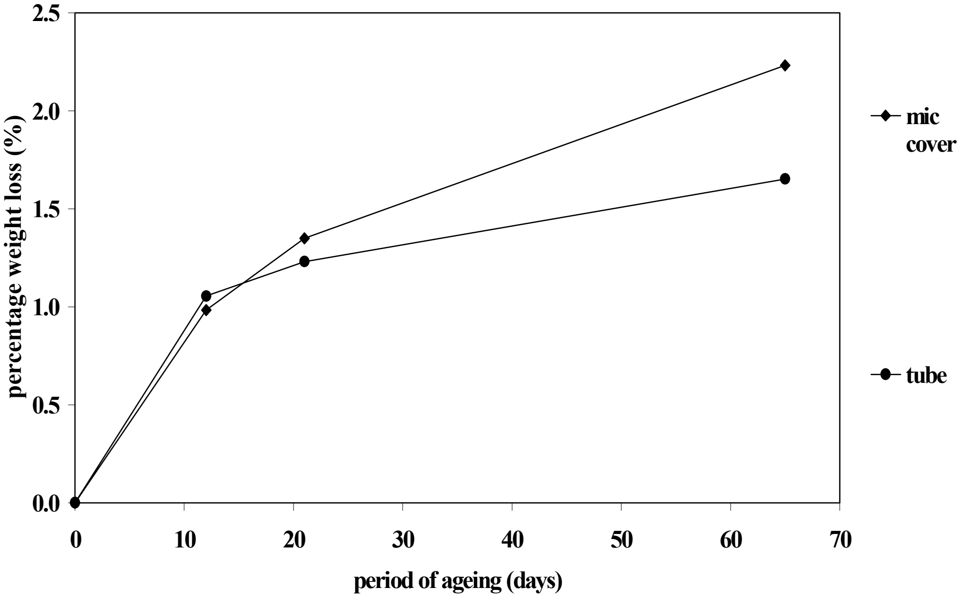
Comparison of mass plasticizer (DEHP plus Eastman TXIB) lost by Solvay model sheets during accelerated thermal ageing in closed environments (upper) and in open oven (lower)

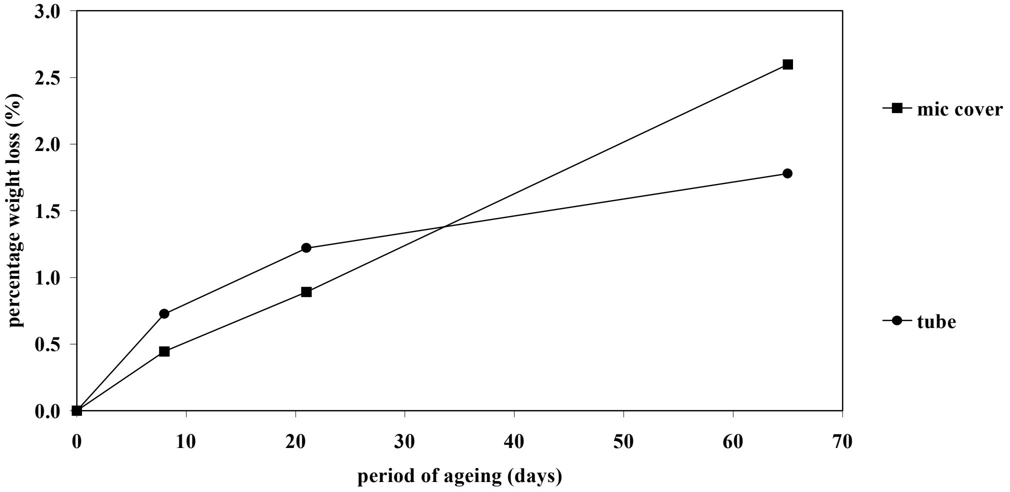


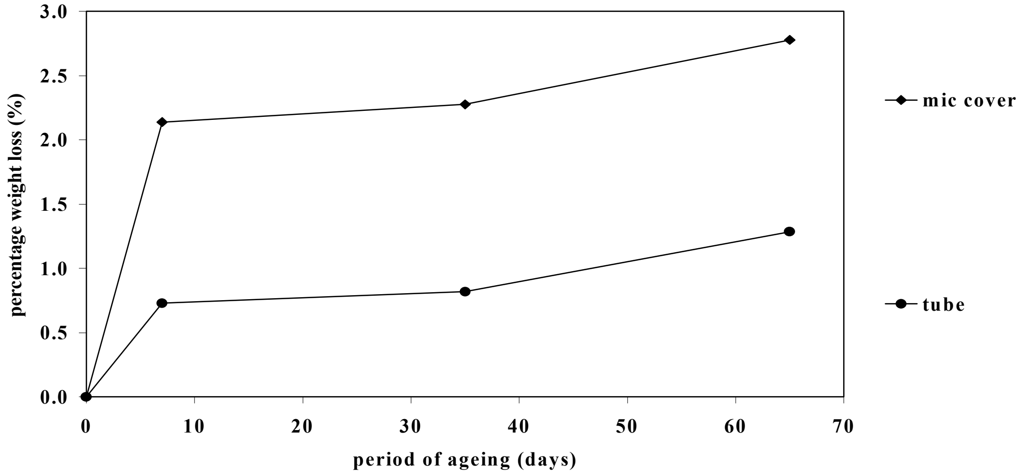
Percentage weight lost by ‘objects’ aged at high RH (upper) in closed environment (middle) and in freezer (lower)



Percentage weight lost by ‘objects’ aged with Ageless oxygen absorber (upper) silica gel (middle) and activated carbon (lower)

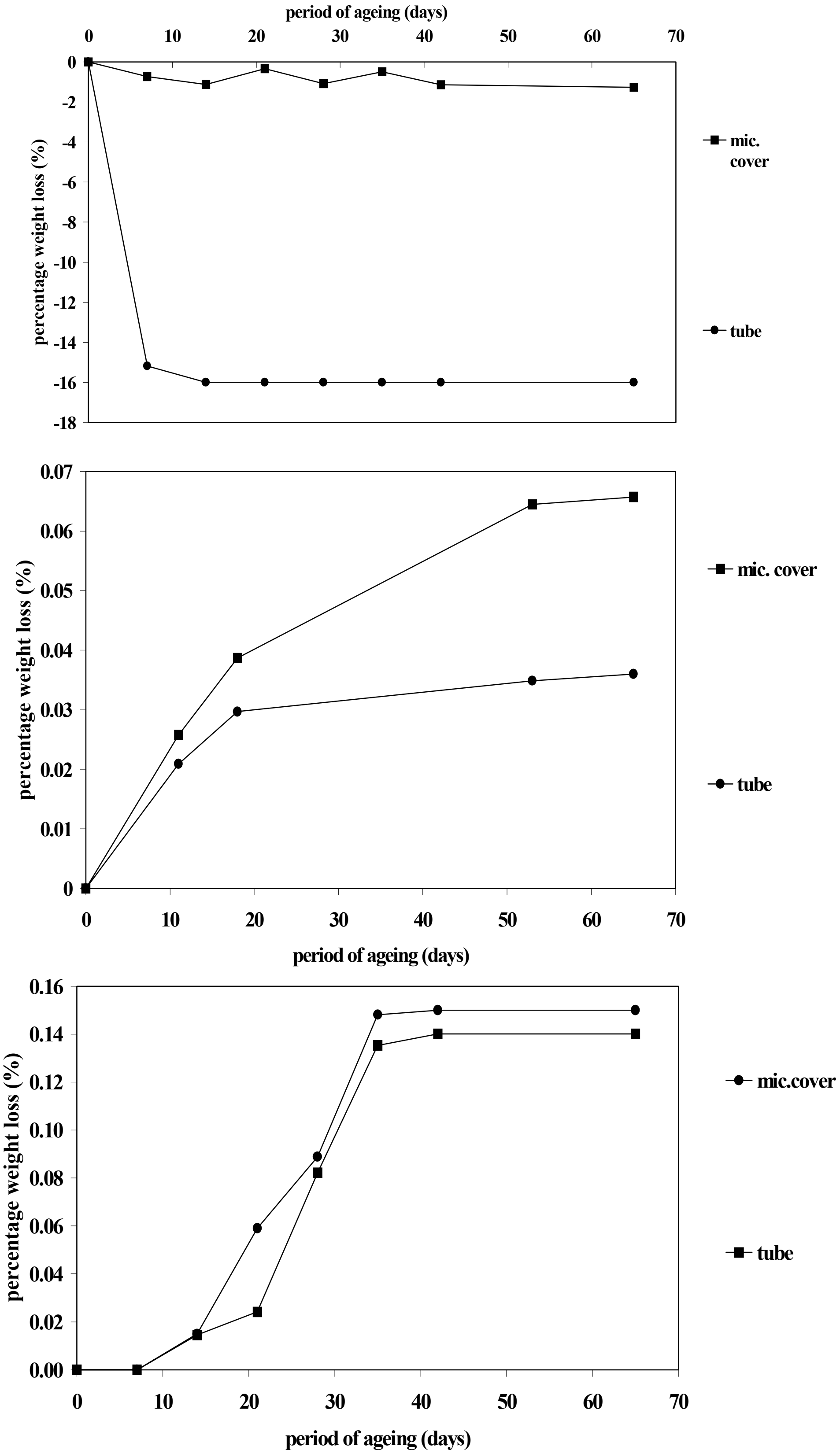




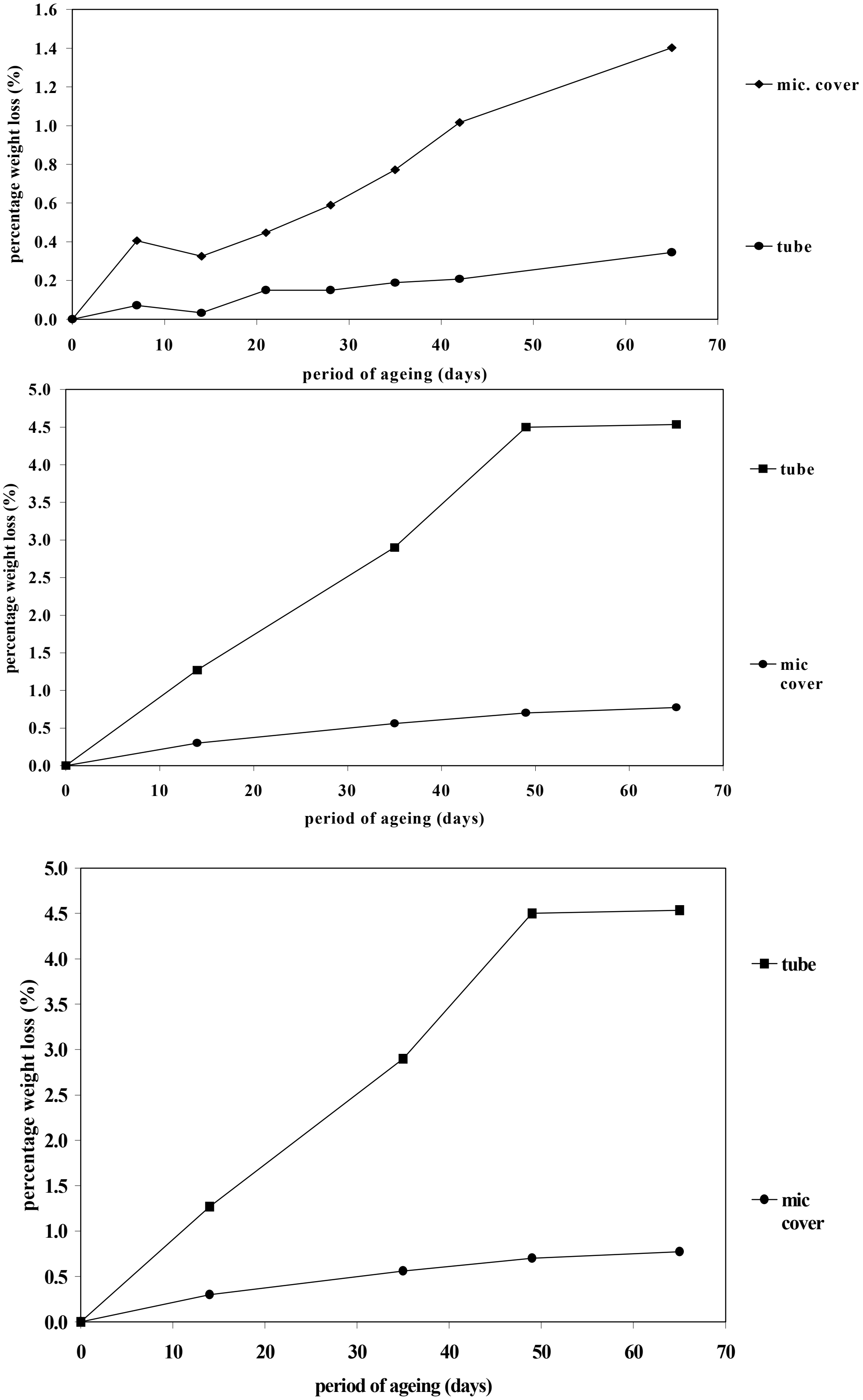


Percentage weight lost by 'objects' aged in open oven (upper) on open glass plate (middle) and in LDPE bags (lower)

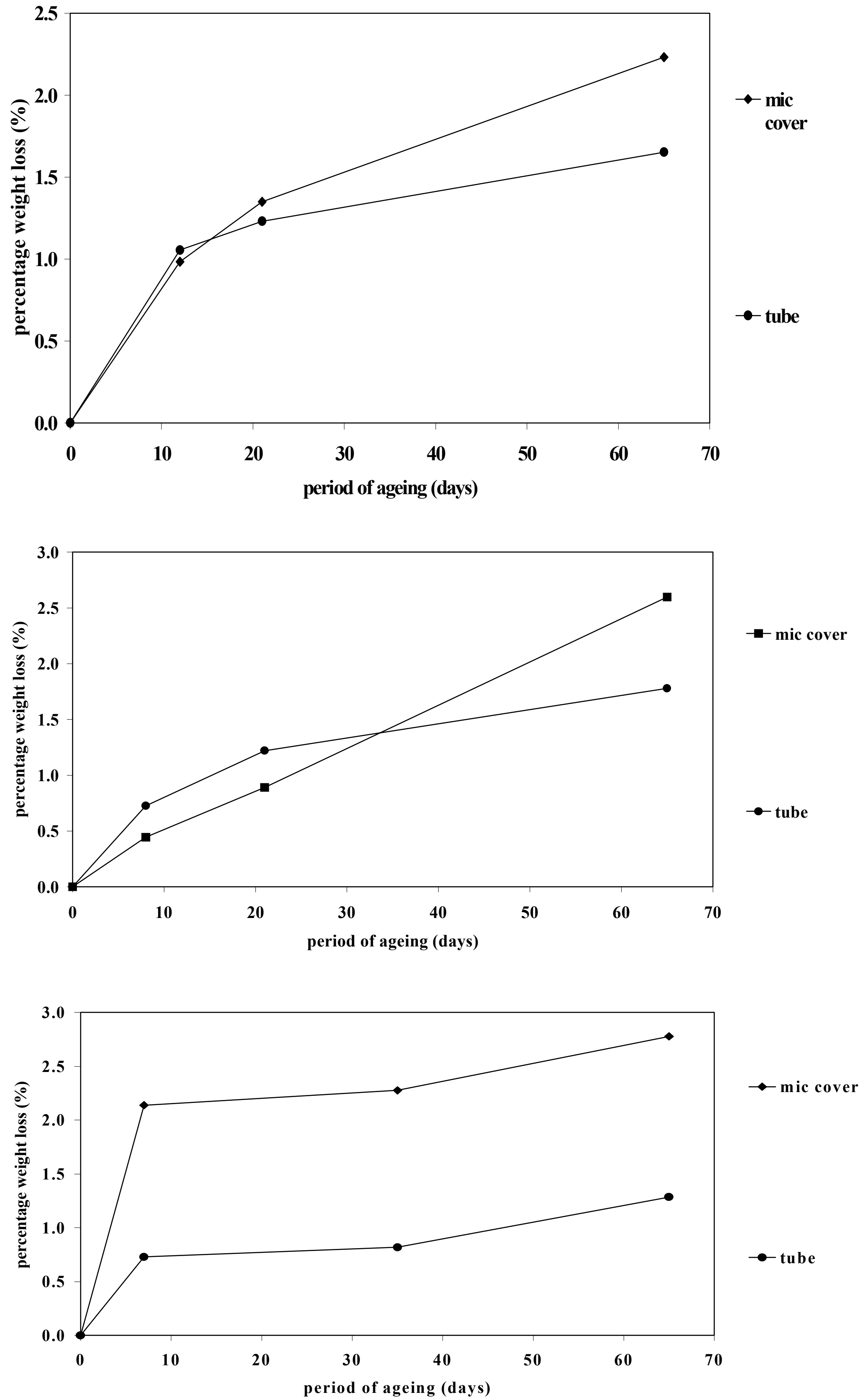
Appendix A3- Weight loss of ‘objects’



Percentage weight lost by 'objects' aged at high RH (upper) in closed environment (middle) and in freezer (lower)

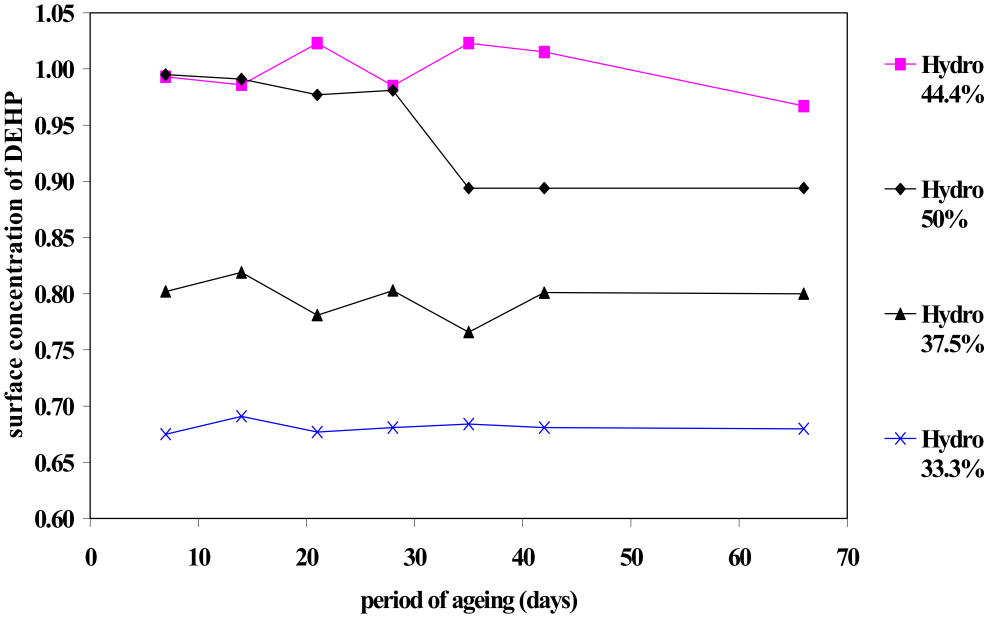


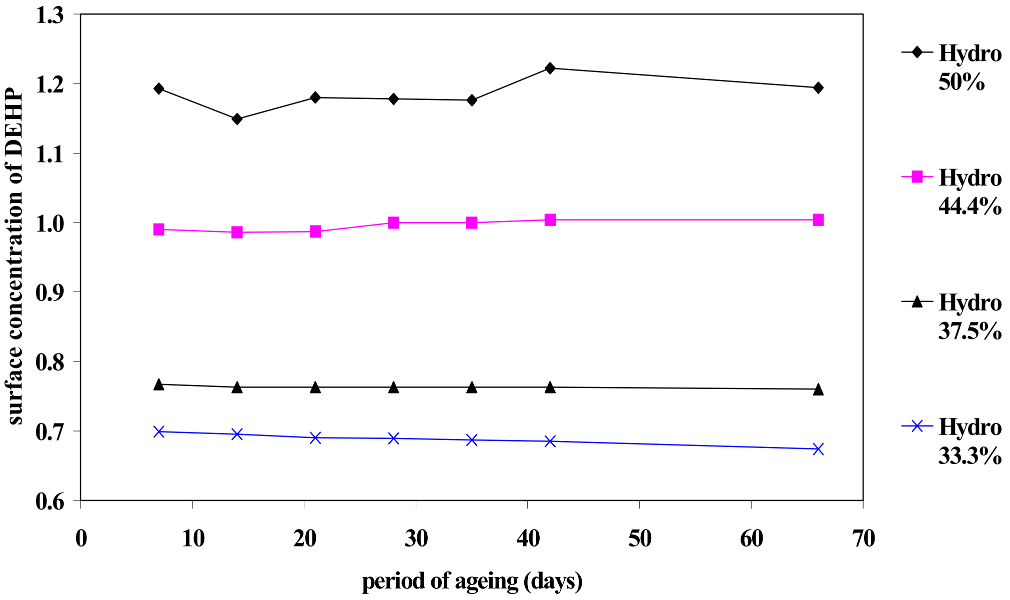
Percentage weight lost by ‘objects’ aged with Ageless oxygen absorber (upper) silica gel (middle) and activated carbon (lower)



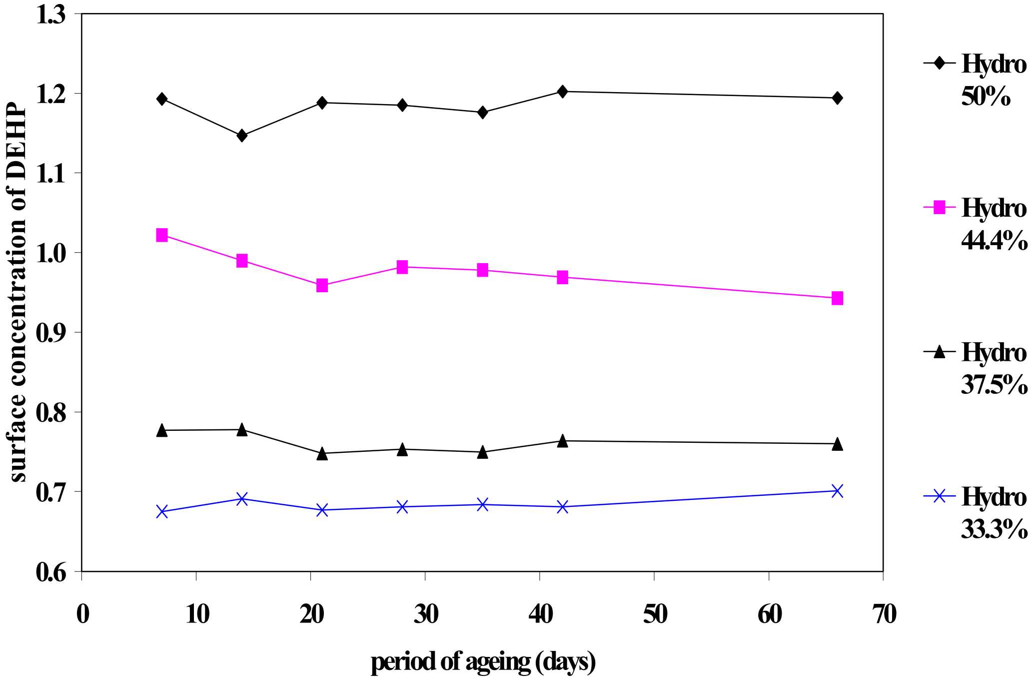
Percentage weight lost by ‘objects’ aged in open oven (upper) on open glass plate (middle) and in LDPE bags (lower)

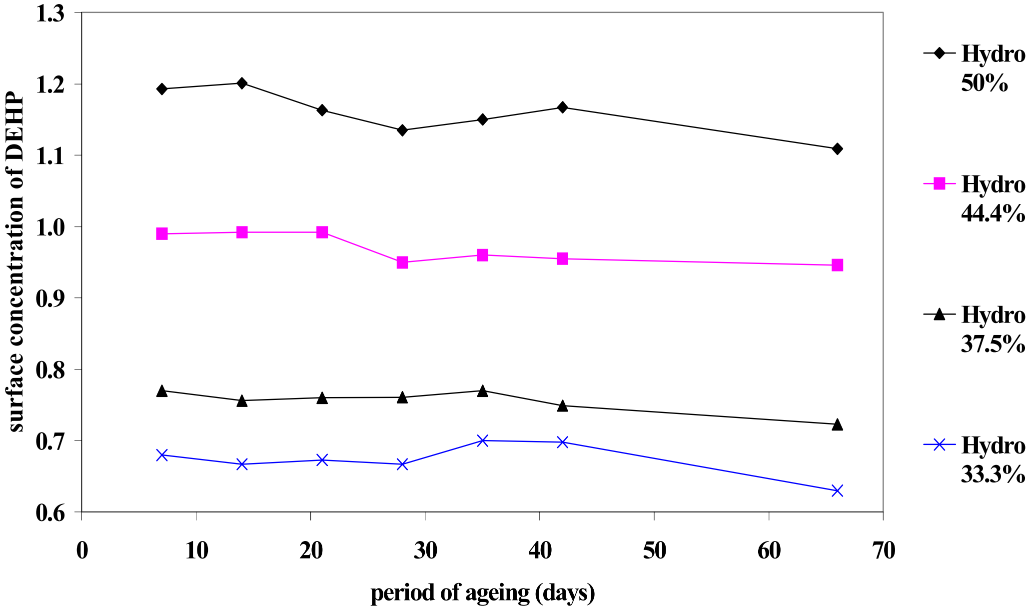
Appendix A3- Weight loss of ‘objects’



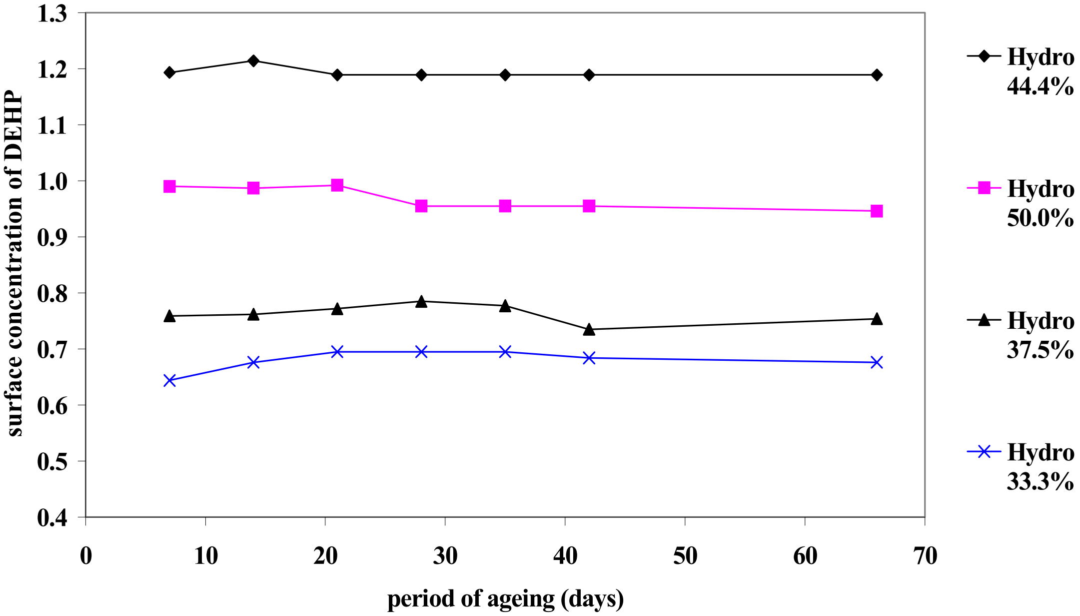


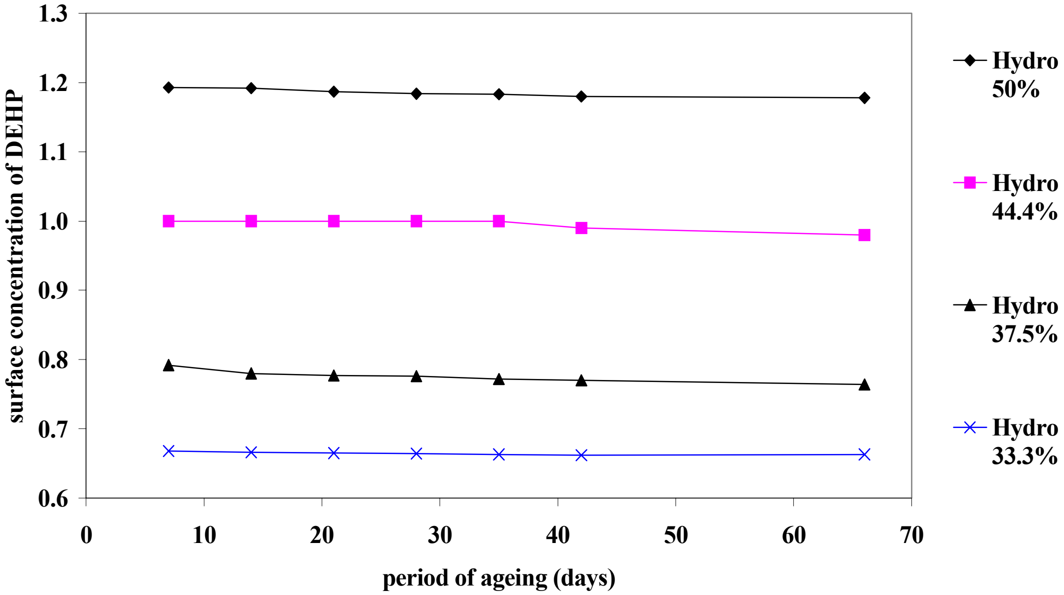
Concentration of DEHP at surfaces of Hydro model sheets aged at high RH (upper) and in closed environment (lower)



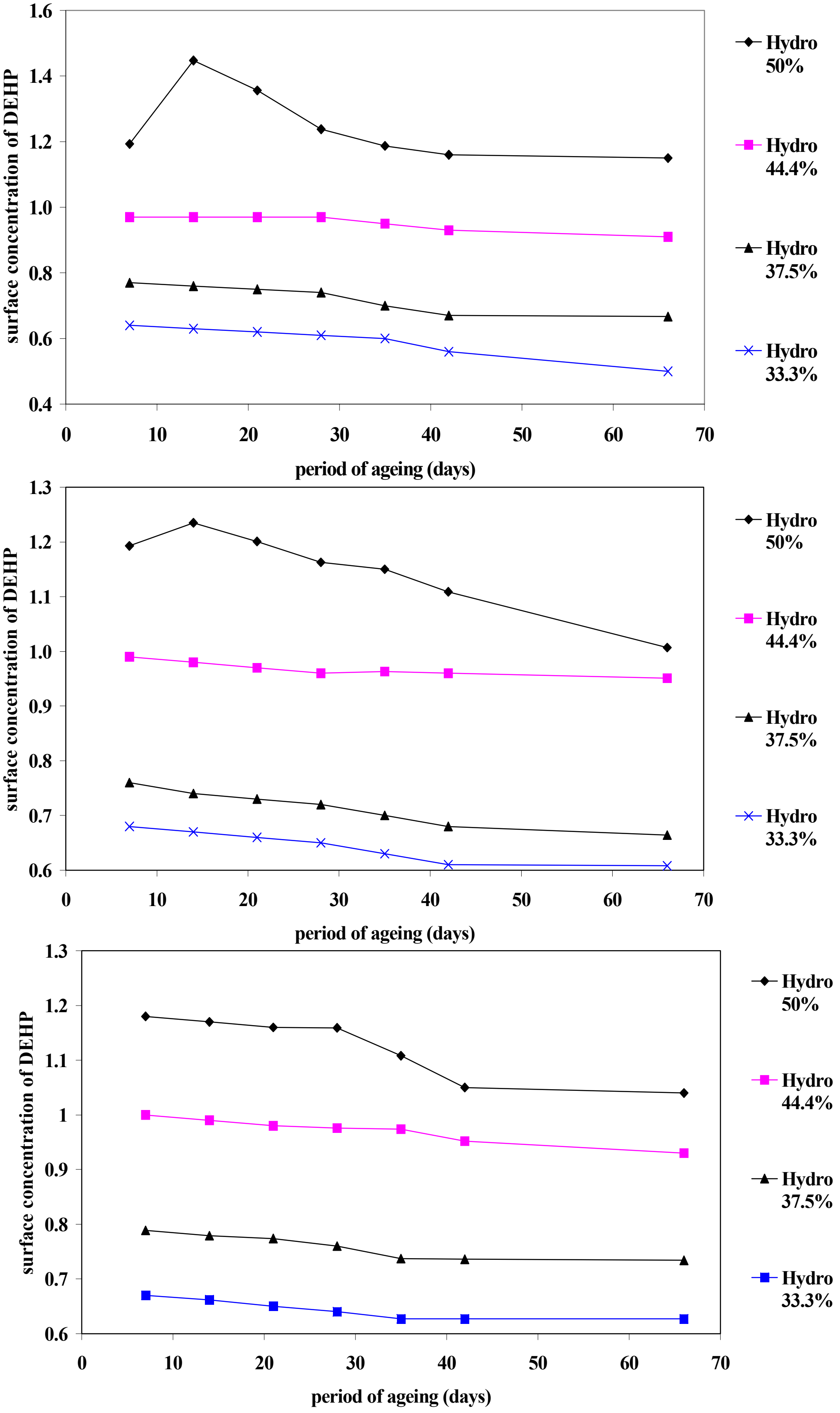


Concentration of DEHP at surfaces of Hydro model sheets aged in freezer (upper) and with Ageless oxygen absorber (lower)

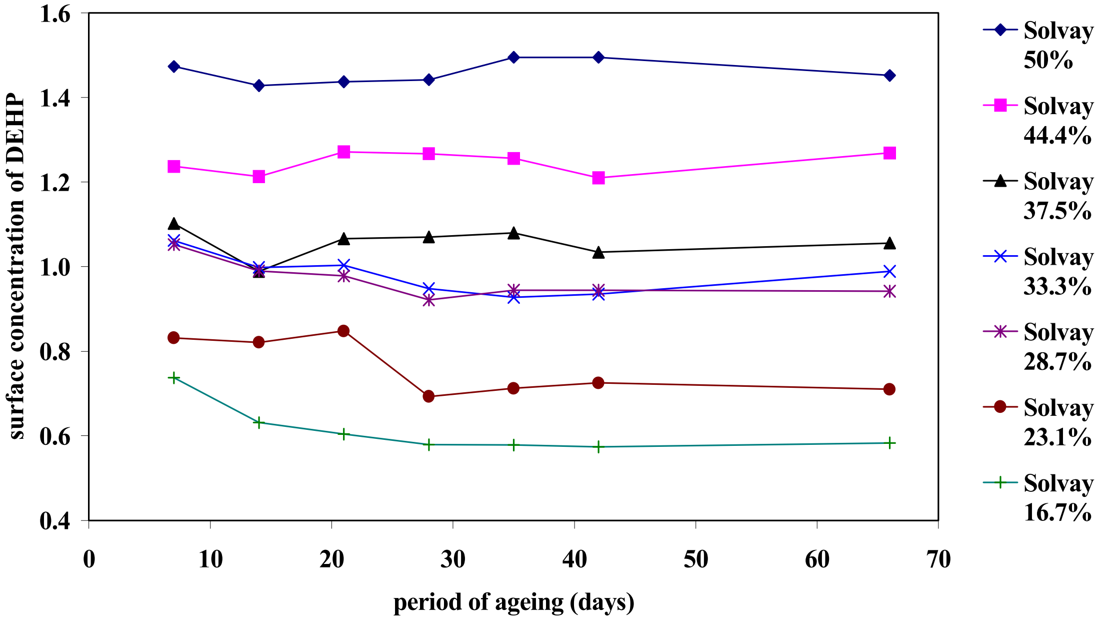


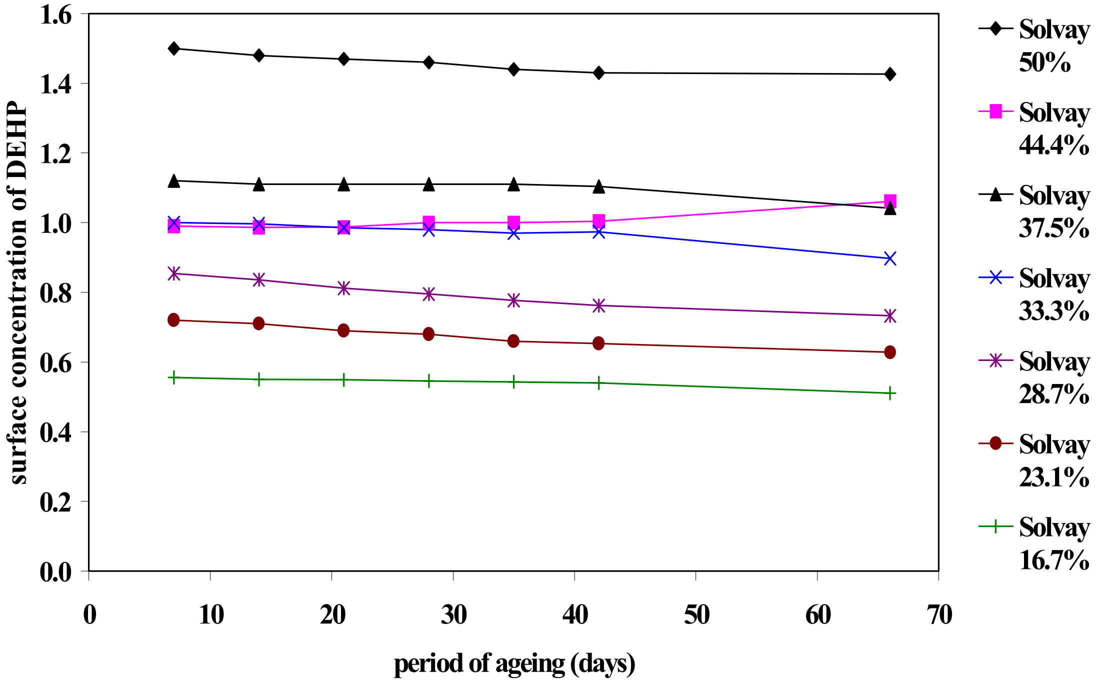


Concentration of DEHP at surfaces of Hydro model sheets aged with silica gel (upper) and activated carbon (lower)

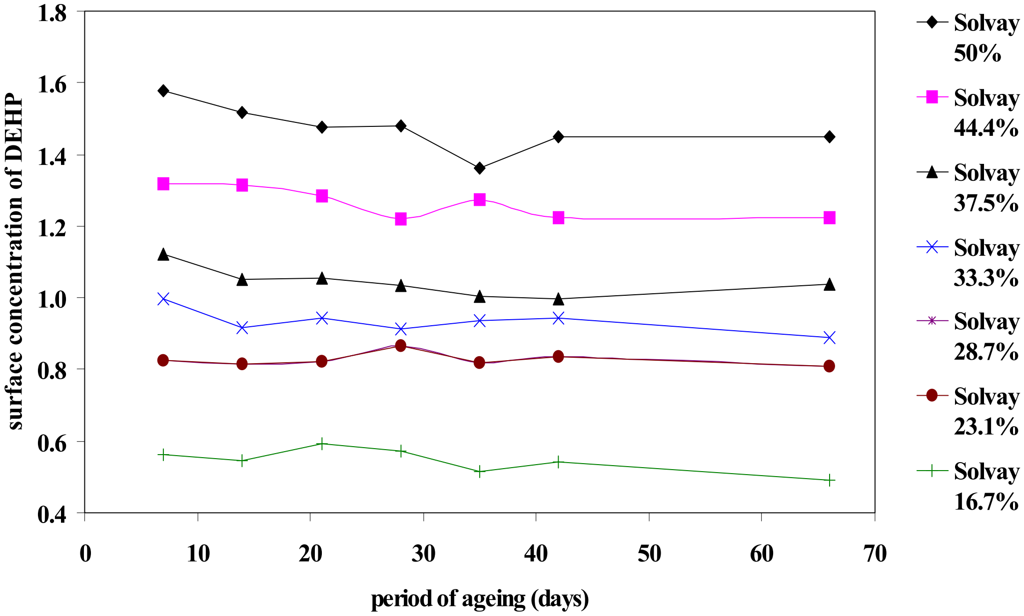


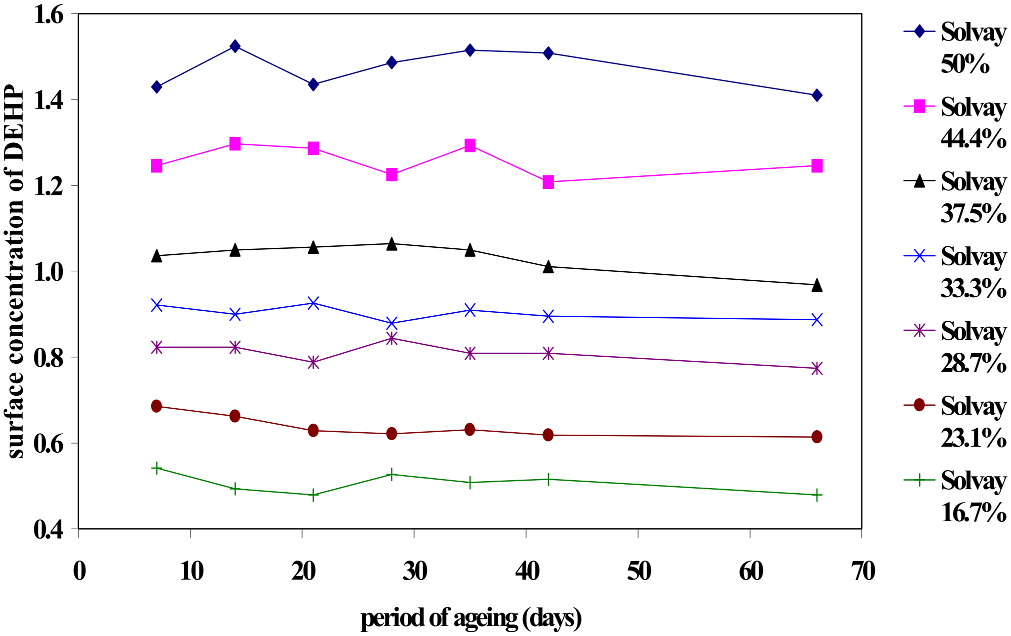
Concentration of DEHP at surfaces of Hydro model sheets aged in open oven (upper) on open glass plate (middle) and in LDPE bags (lower)



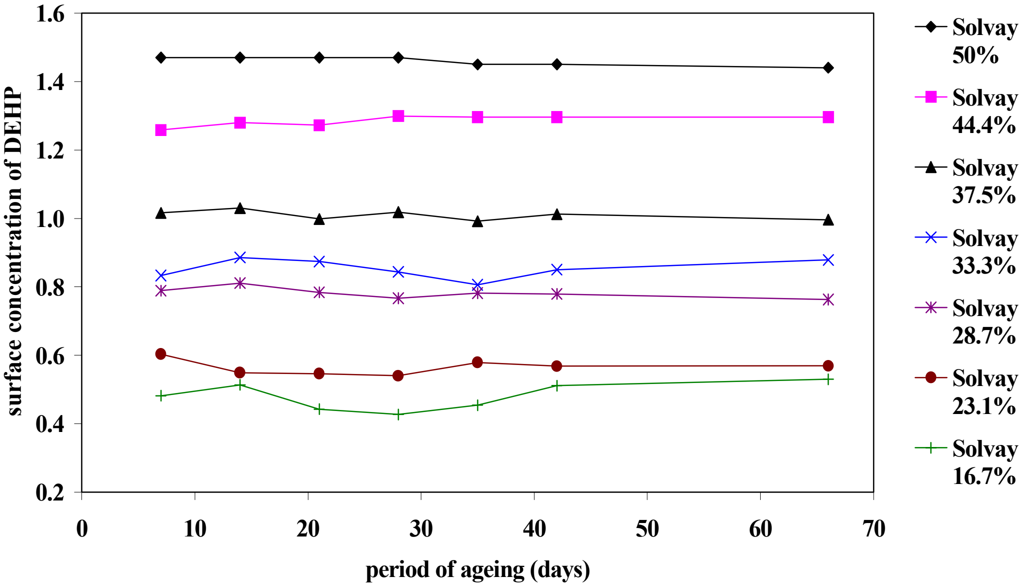


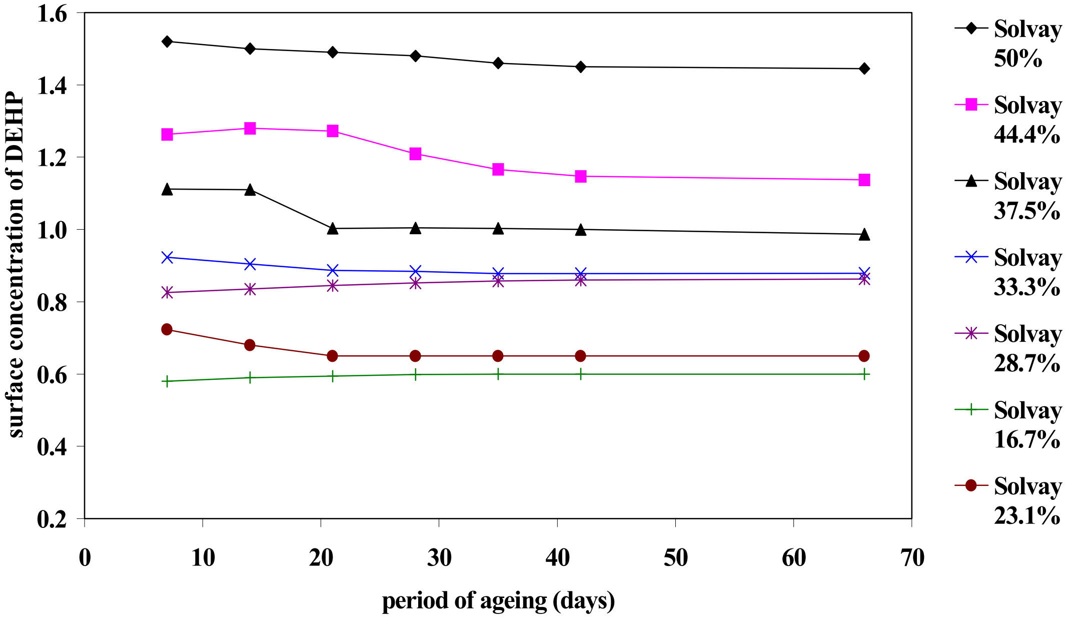
Concentration of DEHP at surfaces of Solvay model sheets aged in closed environment (upper) and freezer (lower)



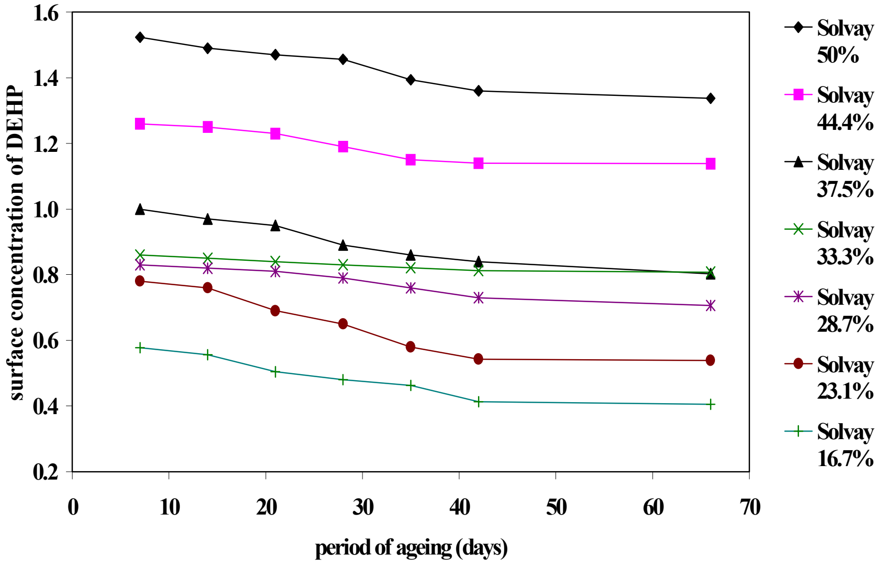


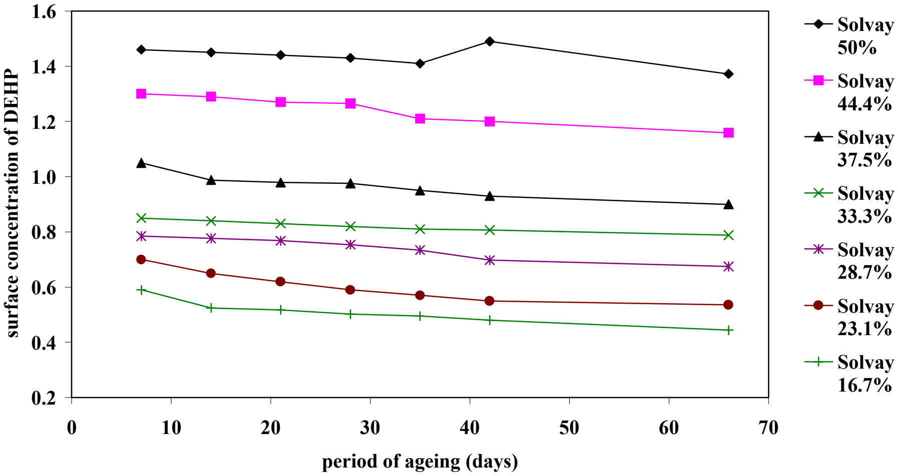
Concentration of DEHP at surfaces of Solvay model sheets aged at high RH (upper) and with Ageless oxygen absorber (lower)

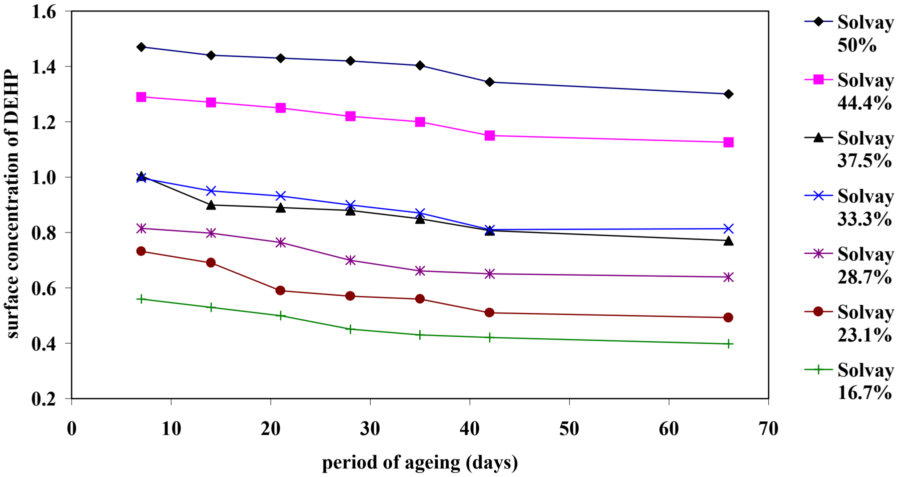




Concentration of DEHP at surfaces of Solvay model sheets aged with silica gel (upper) and activated carbon (lower)







Concentration of DEHP at surfaces of Solvay model sheets aged in LDPE bags(upper) on open glass plate (middle) and in open oven (lower)

Suppliers of chemicals used in the research project

Hydro plastisol and DEHP
Technical Centre PVC, Hydro Polymers Nordic, 3907 Porsgruun, Norway.

Solvay plastisol and Solvic PVC powder
Solvay Chemicals , Rue de Ransbeek, 381, Brussels, Belgium

Eastman TXIB
Bjørn Thorsen A/S, Østerfælled Torv, 14, PO Box 2529, DK-2100 Copenhagen Ø, Denmark.
Tel: +45 35 43 88 43

2-ethyl-1-hexene and 2-ethylhexanol
Greyhound Chromatography, 88 Grange Road West, Birkenhead, Merseyside CH43 4XF, United Kingdom
Tel: +44 151 653 3232
email: info@greyhoundchrom.com

Phthalic acid and phthalic anhydride
Merck KGaA, 64271 Darmstadt, Germany

Silica gel-self indicating
Merck KGaA, 64271 Darmstadt, Germany

Ageless ® oxygen absorber
Mitsubishi Gas Chemical Company Inc., Mitsubishi Building, 5-2 Marunochi 2-chome, Chiyoda-ku, Tokyo 110, Japan

Activated carbon
Prolabo, Merck eurolab, Z.I. de Vaugereau, 45250 Briare le Canal, France