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EFFECTS OF ORGANIC VAPOR ABSORPTION ON PLASTIC PACKAGING

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สุวรรณี สุเมธวาทินกุล : ผลของการดูดซึมไอสารอินทรีย์ต่อบรรจุภัณฑ์พลาสติก (EFFECTS OF ORGANIC VAPOR ABSORPTION ON PLASTIC PACKAGING) อ.ที่ปรึกษา : ศ.ดร.สุดา เกียรติกำจรวงศ์, อ.ที่ปรึกษาร่วม : อ.ดร. สิริวรรณ พัฒนาฤดี, 98 หน้า.

งานวิจัยนี้ศึกษาประเภทของสารอินทรีย์ที่ระเหยได้ และผลของการดูดซึมไอสารอินทรีย์ต่อบรรจุภัณฑ์พลาสติกประเภทพอลิโพรพิลีน และพอลิเอทิลีนเทเรทาเลต พอลิเอทิลีนเทเรทาเลตมีความเป็นผลึกร้อยละ 57 และอุณหภูมิสภาพแก้ว 80 องศาเซลเซียส ซึ่งสูงกว่าพอลิโพรพิลีนที่มีความเป็นผลึกร้อยละ 43 และช่วงอุณหภูมิสภาพแก้ว -5 ถึง 0 องศาเซลเซียส องค์ประกอบหลักของสารระเหยในพอลิพอพิลีนคือ สารประกอบไฮโดรคาร์บอน สารประกอบเอสเทอร์ แนฟทาลีน อนุพันธ์เบนซีน สารประกอบแอลดีไฮด์ สารประกอบคีโตน ฟีนอล และกรดคาร์บอกซิลิก ส่วนประกอบหลักใน พอลิเอทิลีนเทเรทาเลต คือ สารประกอบไฮโดรคาร์บอน สารประกอบแอลกอฮอล์ สารประกอบ แอลดีไฮด์ สารประกอบเอสเทอร์ และสารประกอบเอมีน จากผลการทดลองพบว่าบรรจุภัณฑ์ประเภทพอลิเอทิลีนเทเรทาเลต มีปริมาณสารประกอบไฮโดรคาร์บอน และสารอินทรีย์ที่ระเหยได้น้อยกว่าบรรจุภัณฑ์ประเภทพอลิโพรพิลีน บรรจุภัณฑ์ประเภทพอลิเอทิลีนเทเรทาเลตดูดซึมไอของแอซีโทน โบรโมโพรเพน เฮกเซน โพรพานอลและไทรคลอโรเอทิลีนได้น้อยกว่าบรรจุภัณฑ์ประเภทพอลิโพรพิลีน สมบัติทางกายภาพ และสมบัติทางเคมีของบรรจุภัณฑ์ประเภทพอลิเอทิลีนเทเรทาเลตเปลี่ยนแปลงเพียงเล็กน้อยเมื่อเปรียบเทียบกับบรรจุภัณฑ์ประเภทพอลิโพรพิลีน ภายใต้สภาวะและคุณลักษณะของพอลิเมอร์ที่ทำการทดสอบ

สาขาวิชา...ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์... ลายมือชื่อนิสิต...

ปีการศึกษา...2550............................. ลายมือชื่ออาจารย์ที่ปรึกษา ....

ลายมือชื่ออาจารย์ที่ปรึกษาร่วม.......................

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KEY WORD: ORGANIC VAPOR / ABSORPTION / PLASTIC / PACKAGING

SUWANNEE SUMETWATHINKUL : EFFECTS OF ORGANIC VAPOR ABSORPTION ON PLASTIC PACKAGING.   THESIS ADVISOR : PROF.SUDA KIATKAMJORNWONG, THESIS COADVISOR : SIRIWAN PHATTANARUDEE, 98 pp.

In this research work, the identification of volatile organic compounds (VOCs) and effects of organic vapor absorption on polypropylene (PP) and polyethylene terephthalate (PET) plastic packaging were studied. PET has a higher crystallinity content (57%) and a T_g at 80 ^{o}C, whereas PP has crystallinity of 43% and a T_g range at -5 to 0 ^{o}C.The main compounds detected in PP packaging material are hydrocarbons, esters, naphthalenes, benzene derivatives, aldehydes, ketones, phenols, and carboxylic acids. The main compounds detected in PET packaging are hydrocarbons, alcohols, aldehydes, esters, and amines. The results showed that PET packaging contains much less hydrocarbon and total VOCs than PP packaging. Absorption of acetone, 1-bromopropane, n-hexane, 2-propanol and trichloroethylene vapor in PET packaging were much less than those of PP packaging. Physical and chemical properties of the PET packaging were slightly changed in comparison with the PP packaging under testing condition.

Field of study… Petrochemistry and polymer science… Student's signature...………..................

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LIST OF ABBREVIATIONS

CED	Cohesive Energy Density
^{o}C	Degree celcius
EVOH	Ethylene-vinyl alcohol
FTIR	Fourier Transform Infrared Spectrometer
GC-MS	Gas Chromatograph-Mass Spectrometry
T_g	Glass transition temperature
HDD	Hard Disk Drive
HDPE	High density polyethylene
LDPE	Low density polyethylene
T_m	Melting temperature
N_2	Nitrogen gas
PA-6	Polyamide-6
PET	Poly(ethylene terephthalate)
PP	Polypropylene
PVC	Poly(vinyl chloride)
PS	Polystyrene
SEM	Scanning Electron Microscope
TDS	Thermal Desorption
TG-DTA	Thermogravimetric and Diffrential Thermal Analyzer
TCE	Trichloroethylene
VOCs	Volatile organic compounds

CHAPTER I

INTRODUCTION

1.1   Introduction

In electronic industries, especially in Hard Disk Drive (HDD) production, the improvement of the product quality along with the reduction of the product size are developed. For the HDD quality and reliability, the contamination level of volatile organic (outgas) ionic and solid particulate contaminations[1] should be controlled. For this research, the volatile organic compounds (VOCs) released from HDD during the operations at high temperature are studied. The trouble which originates from contamination has been specified as one of important factors to obstruct the HDD reliability and has caused the read/write error, head disk interference trouble and corrosive attack pole tip surface. The main sources of VOCs are adhesives, solvent, grease, oil, cutting material, plastic packaging that is used in a production process.

Polypropylene (PP) and poly(ethylene terephthalate) (PET) have been wide used in electronic-packaging applications due to its strength, low cost, and ease of processibility. The identification of volatile organic compounds in packaging materials is presented in this study, the majority of the identified compounds are hydrocarbons in polypropylene and poly(ethylene terephthalate). Volatile organic compounds (VOCs) in packaging materials are mostly produced by thermooxidative degradation of polyolefins and polyester in the extrusion coating process. This process is necessary to achieve good adhesion properties, and entails depositing melting polymers on solid surfaces. The combination of high temperatures, often extreme shear stress and the presence of oxygen leads to the formation of organic radicals, and the combination of these radicals produces oxygenated compounds.[2] The

determination of VOCs in polymers by gas chromatography has been usually carried out by purge and trap[3] and direct thermal desorption techniques.[4] Thermal desorption was used in the gas sample preparation technique prior to determination of the volatile organic compounds by gas chromatography-mass spectrometry (GC-MS). By the way, the effect of organic vapor absorption on packaging materials is also presented in this study, because the plastic packaging material can absorb organic vapor from chemicals that are used in the production process. Fourier transform infrared spectrometer (FTIR) was used for the characterization of materials and providing information on the molecular structure of plastic packaging material. Scanning electron microscope (SEM) was used to observe the surface condition of plastic packaging material. Thermogravimetric and differential thermal analysis (TG-DTA) was used for the characterization of thermal property of materials.

1.2 Objectives of the Research work

The objectives of this research include:

1. To study the amount of hydrocarbons released from the plastic material as a guideline for packaging selection of electronic product.

2. To study the effect of organic vapor absorption on plastic packaging.

1.3 Scope of the Research work

This research studies the identification of volatile organic compound in packaging materials. The majority of the identified compound is hydrocarbons in polypropylene and poly(ethylene terephthalate). The low amount of hydrocarbon content in plastic packaging material may involved in a cleanliness control of

electronic parts. The quantitative analysis of hydrocarbon was for the quality evaluation of plastic packaging material. VOCs were purged out from the sample by inert gas and adsorbed onto an adsorption tube. After purging, adsorption tube was heated to release the VOCs for GC-MS analysis.

Furthermore, this research also investigates the effect of organic vapor absorption on plastic packaging material. The types of organic vapors investigated are acetone, 1-bromopropane, n-hexane, 2-propanol and trichloroethylene. All types of them are used in washing and cleaning process of HDD in the Minebea Thai Ltd. In the environment of washing and cleaning process, the organic vapors could be sorbed by the polymer. The relation between absorption time and organic vapor amount is identified. In addition, the characterization of plastic packaging material is also investigated by FTIR, SEM, TG-DTA.

1.4   Content of the Research work

This thesis consists of 5 chapters. The first chapter deals with background, the interest and the scope of this research work. Chapter 2 provides the theory of effect of organic vapor absorption on plastic packaging. Additionally, it includes literature review of previous works that gives beneficial information and trend for the work. The experimental in chapter 3 describes about chemical, equipment, apparatus, and procedure in this work. Chapter 4 describes the results and discussion about characteristic of organic vapor absorption on plastic packaging. Finally, the summary and suggestion for the future work are given in Chapter 5.

CHAPTER II

THEORY

2.1   Functions of packaging

Function of packaging is so obvious as to be overlooked by many, but it is probably the basic function of packaging. With the exception of large, discrete products, all other products must be contained before they can be moved from one place to another. The primary function of the package is to protect its contents from outside environmental effects, be they water, moisture vapor, gases, odors, dust, shocks, vibrations, compressive forces, etc., and to protect the environment from the product. This is especially important for those products such as toxic chemicals which may seriously damage the package environments

The packaging has to perform its functions in three different environments. Failure to consider all three environments during package development will result in poorly designed packages, increased costs, consumer complaints and even avoidance or rejection of the product by the customer. The physical environment is physical damage which can be caused to the product. It includes shocks from drops, falls and bumps; damage from vibration arising from transportation modes including road, rail, sea and air; and compression and crushing damage arising from stacking in warehouses and during transportation, or in the home environment. The ambient environment is the environment which surrounds the package. Damage to the product can be caused as a result of gases (particularly oxygen), water and water vapor, light (particularly UV radiation), and the effects of heat and cold, as well as micro- and macro-organisms which are ubiquitous in many warehouses and retail outlets.

Contaminants in the ambient environment such as exhaust fumes from automobiles and dust and dirt can also find their way into the product unless the package acts as an effective barrier. Human environment is the environment in which the package interacts with people, and designing packages for this environment requires a knowledge of the vision and strength capabilities and limitations of humans, as well as legislative and regulatory requirements. To maximize its convenience functions, the package should be simple to hold, open and use by the consumer. For a product which is not totally consumed when the package is first opened, the package should be able to be resealed and retain the quality of the product until it is completely used. Furthermore, the package should contain a portion size which is also convenient for the intended consumers; a package which contains too large a portion product that it would be deteriorated before being completely consumed.

2.2   Polymer materials for electronic packaging

Polymers are macromolecules built up by the linking together of large numbers of much smaller molecules. The small molecules that combine with each other to form polymer molecules are termed monomers, and the reactions by which they combine are termed polymerization. There may be hundreds, thousands, ten of thousands, or more monomer molecules linked together in a polymer molecule. When one speaks of polymers, one is concerned with materials whose molecular weights may reach into the hundreds of thousands or millions.

It is convenient to divide plastic materials into three classes: thermoplastic polymers, thermosetting polymers, and elastomers.   Thermoplastics can be repeatedly heated to a state of softness where they can be reshaped under low pressure

without degrading the molecular structure. Because the temperatures at which they soften are usually below 150 to 200 ^{o}C, thermoplastics such as polyethylene and nylon are usually restricted from applications involving hot machinery.

Thermosetting polymers are made with resins that crosslink and form chemical bonds between the molecules comprising their structure. This provides greater hardness and strength, and also higher temperature capability in many cases. However, once reacted to form a solid structure, thermosetting plastics cannot be melted and reformed without major property degradation.

Elastomers can be either thermoplastic or thermosetting. Their great flexibility allows them to stretch, flex, and change dimensions with great resiliency. Their primary application is in sealing structural components against fluid leakage.

Thermoplastic polymers can be melt-processed to final shape and dimensions with great accuracy. Plastics almost always comprise polymers with a range of molecular weights, they usually do not have a discrete melting point. Instead, they soften and start flowing with a viscosity which decreases with increasing temperature. Approximate melting temperatures, T_m, for the most common molecular weight members of the polymeric structures. In the case of polymers which can align their chains into crystalline domains, the glass transition temperature, T_g, defines the temperature above which crystallinity disappears.

The materials used for the investigations described in this thesis were chosen as below because of their common use as electronic packaging materials and their different material characteristics.

Polyolefins

A polyolefin is a polymer produced from a simple olefin, or alkene as a monomer. For example, polyethylene is the polyolefin produced by polymerizing the olefin "ethylene". An equivalent term is polyalkene; this is a more modern term, although polyolefin is still used in the petrochemical industry. Polypropylene is another common polyolefin which is made from propylene.

Polypropylene

Polypropylene (PP) is a linear polymer containing little or no unsaturation. The basic structural unit of PP is shown in Figure 2.1, together with atactic PP where the methyl groups are randomly distributed on either side of the chain, an event which arises when polymerization occurs in the absence of stereospecific catalyst. This non-crystalline material has a density of about 850 kg m^{-3} and is soft, tacky and soluble in many solvents. It finds use in hot-melt adhesives. The most regular crystalline polymer produced by stereospecific catalysts is known as the isotactic form, the name stemmimg from the original idea that the methyl groups are always above or below the horizontal plane. In fact, the carbon atoms arrange themselves into a helical chain with the methyl groups on the outside. Isotactic PP is never perfectly stereoregular, the degree of isotacticity varies from 88-97 %. Two other forms are the syndiotactic where the methyl groups alternate above and below the horizontal plan, and stereo-block where the blocks of methyl groups are alternately above and below the horizontal plane. The regular helices of the isotactic form can pack closely together, whereas the atactic molecules have a more random arrangement. Atactic PP is an amorphous, rubbery material of little value, whereas the isotactic PP is stiff,

highly crystalline and has a high melting point. In commercial polymers, the greater the amount of isotactic material, the greater the crystallinity and thus the greater the softening point, tensile strength and hardness, all other structural features being equal. PP has a lower density (900 kg m^{-3}) and a higher softening point (140 – 150°C) than the polyethylenes, low water vapor transmission, medium gas permeability, good resistance to greases and chemicals, good abrasion resistance, and high temperature stability, as well as good gloss and high clarity, the latter two factors making it ideal for reverse printing. Although free from environmental stress cracking problems, it is more susceptible to oxidative degradation at elevated temperatures, necessitating the inclusion of antioxidants in all commercial PP compounds. Whereas polyethylene cross-links on oxidation, PP degrades to form lower molecular weight products. A similar effect is observed when PP is irradiated. The molecular structure of PP in demonstrated in Figure 2.1.

$$\left[CH_2 - \underset{\underset{CH_3}{|}}{CH} \right]_n$$
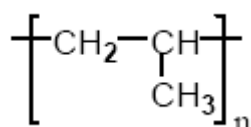
Figure 2.1 Molecular structure of PP.

These methyl groups greatly restrict molecular rotation and flexibility, PP molecules coil due to the regularity of the methyl groups and flexibility of the backbone. These coils crystallize to high degree leading to excellent chemical solvent resistance and opacity. Isotactic polypropylene (i-PP) has the lowest density (900-910 kg m^{-3}) of the major plastics and processes a very high strength : weight ratio. It has a high crystalline melting point of 165-175 ^{o}C and is usable to 120 ^{o}C; both temperatures are higher than the corresponding values for HDPE.

Polyesters

Polyesters have hydrocarbon backbones containing ester linkages, hence the name. The ester groups in the polymer chain are polar, with the carbonyl oxygen atom having a somewhat negative charge and the carbonyl carbon atom having a somewhat positive charge. The positive and negative charges of different ester groups are attached to each other. This allows the ester groups of nearly all chains to line up with each other in a crystal form.[5] Polyesters are based on carbon-oxygen-carbon links, where one of the carbons is part of a carbonyl group, and are formed by the process of condensation polymerization. In this process, two molecules are joined together through the elimination of a smaller molecule (typically H_2O) whose atoms derive from both the parent molecules. Simple polyesters are derived from condensation of a polyhydric alcohol and a polyfunctional acid and are sometimes described as alkyds (from alcohol and acid). Each –COOH, -NH_2 per molecule of 2 to form a linear chain, while if one (or both) monomers have a functionality of at least 3, cross-linkage can occur resulting in a much more rigid 3-D lattice structure. The three most important types of polyesters are poly(ethylene terephthalate), poly(ethylene naphthalate), and polycarbonate.

Poly(ethylene terephthalate)

Poly(ethylene terephthalate) (PET) is produced by a condensation reaction of ethylene glycol and terephthalic acid or dimethyl terephthalate. The molecular structure of PET is given in Figure 2.2.
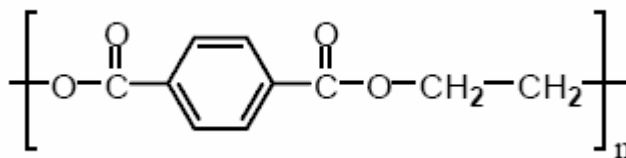
Figure 2.2 Molecular structure of PET.

PET has a T_m of 267°C and a T_g between 67°C to 80°C. PET film's outstanding properties as a food packaging material are its great tensile strength, excellent chemical resistance, light weight, elasticity and stability over a wide range of temperatures (-60 to 220°C). A fast-growing application for PET is "ovenable" trays for frozen food and prepared meals, where they are preferable to foil trays because of their ability to be microwaved without the necessity for an outer board carton. These trays are thermoformed from cast PET film and crystallized (the material then being referred to as CPET), the crystallization heat-setting the tray and preventing deformation during cooking and serving. Because of its rather high T_g, only a limited amount of crystallization can occur during cooling after injection molding of PET. Such amorphous moldings are of little value. When they are heated above 80°C crystallization can occur and they show considerable distortion, shrinkage and clouding.

PET has outstanding properties that make it valuable to the converting and packaging industries. PET film offers mechanical strength, dimensional stability, moisture resistance, chemical resistance, clarity, stiffness, and barrier properties. It is easy to handle and can be printed or laminated.[6]

The combination in the extruder high temperatures, frequent extreme mechanical stresses and the presence of oxygen causes the degradation of polymer.[7,8]

The mechanism of thermooxidative degradation highlights the presence of alkyl radicals that combines with oxygen alkoxy and peroxy radical[8,9]. The combinations of these radicals produce volatile organic compounds (VOCs) such as hydrocarbons, alcohols, aldehydes, ketones and carboxylic acid.[10-12] The VOCs formed during a extrusion-coating process can migrate to the materials contained in the packaging and changed their organoleptic properties imparting undesirable odours and flavours. The factors that determine the migration are mainly the temperature, the contact time, the equilibrium constant, the concentration, the solubility and the diffusion coefficient.[13] The diffusion of molecules through polymer membranes is an important phenomenon in many different areas of science and engineering. For example, the diffusivity in polymer films and membranes is important in the use of polymers in packaging applications. [14,15] In fact, when a plastic packaging material is in contact with any product mass transfer occurs: migration of additives, necessary for the stability and the processing of the packaging, into the packed product could occur and, conversely, the product components (small molecules, aromas, flavour) could be sorbed by the polymer.[16,17]

In the literature [18-24], the transport properties of small molecules in polymers (sorption of solvent) depend on several factors:

1.   the chemical structure of the packed product: acid, amide, ester, etc.,

2.   characteristics of the polymer (the container): molecular weight, degree of crystallinity, glass transition temperature, and so on,

3.   the temperature of the environment,

4.   the size, the shape and the polarity of diffusing molecules, [22]

These factors essentially control the solubility and the degree of swelling of

the diffusing molecules and influence the rate at which these molecules are sorbed and transport into the polymer. [25]

2.3 Additives for plastics

The appropriate grade of isotactic polypropylene (PP) and poly(ethylene terephthalate) (PET) is not processable and durable without additives. Scientific development of various categories of additives enabling these plastics to suit particular applications was exploited commercially under stringent legislation and environmental rules. Some additives, residues or processing aid remain in trace amounts in the plastics. Some of the additives, stabilizers in particular, are very reactive and are present in the plastic matrix in a chemically transformed form. When considering mass transport phenomena in the plastics packaging which contact with the product, specific attention must be paid to possible transfer of residue monomers, oligomers, processing aids, and additives, mostly low-molecular weight compounds, from the plastics.

Nucleating agents

To achieve consistent properties and morphology of semicrystalline plastics, nucleating agents are added to trigger a heterogeneous nucleation of the plastic melt and to give crystals of regular size. Sodium salts of organophosphates, salt of benzoic or phthalic acid, some organic compounds, e.g. sorbitol bis (3,4-dimethylbenzylidene diacetal) or very finely ground fillers (clays, silica) are used in PP in amount 0.1 – 0.3 %. Analogous agents may be used in PET.

Lubricants

By adding lubricants, the melt rheology of plastics is affected, whereas processing above the glass transition temperature is improved due to the decrease of external friction. Lubricants applied to the outer surface of the polymer melt are effective on plastics/processing equipment interfaces and internal friction. Lubricants added into the polymer mass are effective on macromolecule/macromolecule interfaces and improve polymeric chain movements. Typical lubricants are fatty alcohols, fatty acids, their esters with fatty alcohols, glycerol or pentaerythritol, amides, acids, diesters of phthalic acid, paraffin wax, and polyethylene wax.

Antistatic agents

Typical ionic agents that are used as external antistats are cation-active [quaternary ammonium, phosphonium or sulfonium salts, e.g. (3-dodecanoylamidopropyl) trimethylammonium methylsulfate] and anion-active [e.g. alkylsulfonate or salts of alkylated benzenesulfonic acid]. Non-ionic agents [such as poly(ethylene glycol)-monoethers or ethoxylated fatty alkylamines] are used as internal antistats. Concentration of antistats in plastics is mostly 0.1 to 2 % weight.

Stabilizers

Plastics are rather different as far as their inherent sensitivity to degradation is concerned. Differences in sensitivity are due to their chemical structures, i.e. presence of characteristic degradation-sensitive moieties in polymer construction units, defect structures (structural inhomogeneities) present in unpredictable amounts and/or formed as a consequence of adventitious oxidation during manufacture, storage and

sensitizing degradation during processing and subsequent application. The level of structural inhomogeneities sensitizing the degradation of plastics increases gradually during the polymer lifetime. Chain scission, branching or crosslinking and the formation of new functional groups, such as olefinic unsaturation C=C and polymer-bound oxygenated groups (hydroxyl, carbonyl, carboxyl) are chemical consequences. Others are discoloration, loss of gloss or transparency, formation of surface cracks, and undesirable changes in mechanical properties (elongation, tensile and impact strengths). Antioxidants are added to polymers to prolong their useful lifetime. Antioxidants protect plastics against thermal oxidation. Phenols and dialkyl hydroxylamines antioxidants are effective for thermal stabilization of polyolefins such as PP and styrene-based polymers. Common concentrations in plastics range between 0.025 and 0.3 % weight. Organic compounds of trivalent phosphorus are excellent processing stabilizers for polyolefins and are commonly used in combinations with phenolic antioxidants. Phosphites are used in PET and polyolefins in the level of 0.05 – 0.3 % weight.

2.4   Solubility parameter

The basic equation of Hildebrand and Scott designated the energy of vaporization as the cohesive energy density (CED) and it's square root as the solubility parameter, (δ) is shown in Equation (2.1),

$$\delta = \frac{(\Delta H_v - RT)^{1/2}}{V} = \frac{(\Delta E_v)^{1/2}}{V} = (ced)^{1/2} \qquad (2.1)$$

This equation is simply stating that the heat of vaporization H_v less the volume work,

where R=gas constant, T=absolute temperature. RT is an estimate of energy to maintain the liquid state or cohesive energy. Dividing this value by molar volume V corrects for density leading to the term cohesive energy density. The values are reported in $MPa^{1/2}$ units. This equation is only suitable for vapors obeying the ideal gas law ie: nonpolar fluids (nonelectrolytes). An area of somewhat generalized agreement was the consideration that polar (aqueous and nonaqueous electrolytes) fluids had three major intermolecular forces to consider:

Dispersion (London) force "D"-common in all cohesive energy

Hydrogen bonding "H", now referred to as H-bonding

Dipole moment "P", a measure of the polar (electrostatic) aspect of a molecule.

The Hansen modification, utilizing these three intermolecular attractions, as shown in Equation (2.2):

$$\delta^2 = \delta_D^2 + \delta_P^2 + \delta_N^2 \tag{2.2}$$

was intended for polar fluids by assigning a partial solubility parameter equal to the square root of the corresponding partial cohesive energy density. The gasoline-ethanol combination previously noted was an exothermic (gave up heat) mixture. Jensen correctly noted that Equation (2.2) contains only the squares of the difference, it can thus only lead to positive or endothermic values and is therefore incapable of predicting accurately nonideal fluid/elastomer interactions (square of two negatives is a positive). This lack of consistency was previously noted by Hertz.

The solubility parameter of the solvents and the polymers is included in Table 2.1. The solvent with solubility closed to that of the polymer tends to interact or possibly dissolve such polymer.

Table 2.1 The solubility parameter of solvents**.**

Solvent	Solubility parameter $(MPa)^{1/2}$
Acetone	19.7
1-bromopropane	18.2
Hexane	14.9
2-propanol	23.5
Trichloroethylene	18.7

Note: the solubility parameters of PP and PET are 15.76 and 21.5 $(MPa)^{1/2}$, respectively

2.5 Organic vapor-electronic packaging interaction

2.5.1 Permeation, migration and absorption

Interactions within a package system refer to the exchange of mass and energy between the packaged product, the package material and the external environment. Product-packaging interactions can be defined as an interplay between product, packaging, and the environment, which produce an overall effect on the product, and/or the package.

Mass transfer processes in packaging systems are normally referred to as permeation, migration and absorption (Figure 2.3). Permeation is the processes resulting from two basic mechanisms: diffusion of molecules across the package wall, and absorption/desorption from/into the internal/external atmospheres. Migration is the release of compounds from the plastic packaging material into the product.[26] The migration of compounds from polymer packaging materials might be caused by the leaching of residues from the polymerisation (e.g. monomers, oligomers, solvents),

additives (e.g. plasticizers, colourants, UV-stabilisers, antioxidants) and printing inks. Later, absorption or scalping of components originally contained in the product by the packaging material attracts attention. Product components may penetrate the structure of the packaging material, causing loss of aroma, or changing barrier and/or mechanical properties, resulting in a reduced perception of quality.[27]

Environment	Polymer film	Foodstuff	Migrating substances	Adverse consequences
(1) (2)		PERMEATION	Oxygen Water vapour Carbon dioxide Other gases	(1) Oxidation Microbial growth Mold growth Off-flavour (2) Dehydration Decarbonation
		MIGRATION	Monomers Additives	Off-flavour Safety problems
		ABSORPTION (SCALPING)	Aroma compounds Fats Organic acids Pigments	Loss of aroma intensity Development of unbalanced flavour profile Damage to the package

Figure 2.3 Possible interactions between product, polymer film and the environment, together with the adverse consequences.[28]

2.5.2 Odor Permeability

The permeability of packaging materials to organic vapors is of considerable interest, particularly where the package contents have to be protected against contamination from foreign odors or where there is a requirement to ensure that volatile flavoring materials are not lost from the package. Although the permeabilities

of the permanent gases and of water vapor through many packaging materials are well known, there is a lack of data for the permeation of organic vapors. For gases, the permeability coefficient which is independent of concentrations can be reliably extrapolated to predict permeation rates where there are low concentration gradients across the barrier. However, in the case of many organic vapor/packaging film combinations, the permeability coefficient is strongly dependent on concentration. This effect occurs because the vapor interacts with and swells the polymer and increases the permeation rate. When exposed to certain saturated vapors, this effect can be so extreme as to cause distortion of the film, resulting in very high permeation coefficients, limited principally by the rate at which the vapor is removed from the surface of the film. There are no standard tests for the measurement of odor permeability. As with permeability studies of the permanent gases, procedures to study organic vapor permeability include the isostatic and quasi-isostatic methods.

2.5.3 Mass transport processes

The fundamental driving force in the transfer of components through a package system is the tendency to equilibrate the chemical potential.[26] Mass transport through polymeric materials can be described as a multistep process (Figure 2.4). First, molecules collide with the polymer surface. Then they adsorb and dissolve into the polymer mass. In the polymer film, the molecules 'hop' or diffuse randomly as their own kinetic energy keeps them moving from vacancy to vacancy as the polymer chains move. The movement of the molecules depends on the availability of vacancies or 'holes' in the polymer film. These 'holes' are formed as large chain segments of the polymer slide over each other due to thermal agitation. The random

diffusion yields a net movement from the side of polymer film that is in contact with a high concentration or partial pressure of a permeant to the side that is in contact with a low concentration of the permeant. The last step involves desorption and evaporation of the molecules from the surface of the film on the downstream side.[29] Absorption involves the first two steps of this process, i.e. adsorption and diffusion, whereas permeation involves all three step.[30]
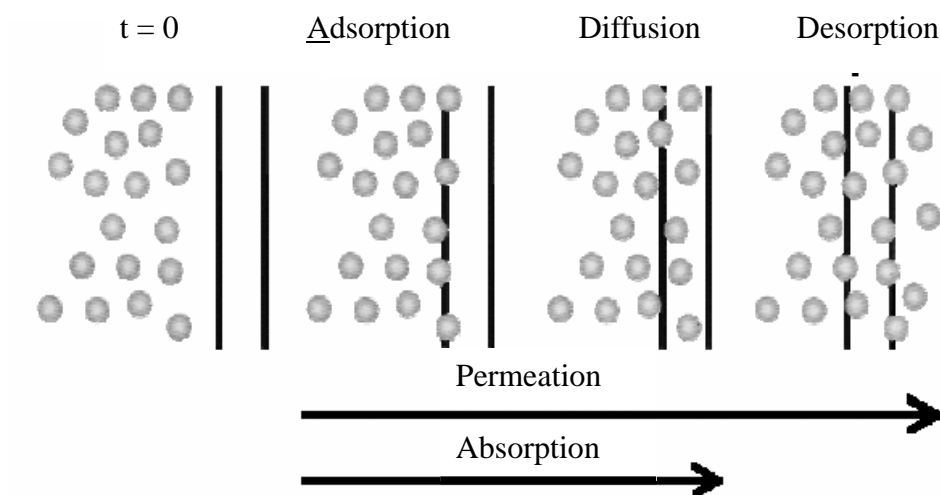
Figure 2.4 Mass transport of molecules through a plastic polymer film.

In virtually every case, the permeation of gases and vapors through non-porous membranes is controlled by the solution and diffusion steps. The diffusion coefficient, D, is a measure of the speed of molecules moving in the polymer. The solubility coefficient, S, is an indication of the number of permeant molecules that are diffusing. Together, the diffusion coefficient and the solubility coefficient describe the permeability coefficient, P.[30]

$$P = D \text{ x } S \qquad\qquad (2.3)$$

Equation(2.3) is applicable only for situations where D is independent of permeant

concentration c and S follows Henry's law of solubility as shown in Equation (2.4)

$$c = Sp \tag{2.4}$$

where p is the partial pressure of the penetrant.

Mass transport is described by Fick's first law (Equation 2.5) which relates the flux to the driving force:

$$Q = -D\frac{\partial C}{\partial x} \tag{2.5}$$

where Q is the flux of permeant per unit area and x is the length.

By combining Equation (2.3, 2.4 and 2.5), the steady state rate of permeation through a polymer film with a cross-sectional area A and thickness L can be given by Equation (2.6),

$$\frac{\Delta M_x}{\Delta t} = \frac{PA\Delta p_x}{L} \tag{2.6}$$

where M is the quantity of permeant x, t is time, and Δp_x is the difference in partial pressure of the permeant on two sides of the film.[30]

Although there are similarities between gaseous and liquid transport in a polymer, there are also a number of differences. In general, the affinity between liquids and polymers is much greater than that between gases and polymers, i.e. the solubility of a liquid in a polymer is much higher than that of a gas. Another difference between liquids and gases is that gases in a mixture permeate through a polymer in quite an independent manner, whereas with liquid mixtures the transport of the components is influenced by thermodynamic interaction (such as solubility and

polarity).[31] When the permeation process involves highly interactive organic penetrants such as aroma, flavour, or solvent molecules, the diffusion process is more complex than the diffusion of simple gases, and the diffusion coefficient may vary as a function of penetrant concentration and time. Fick's second law (Equation 2.7), which is derived from Fick's first law, describes the non-steady state where the concentration gradient is a function of distance x and time t, if the diffusion coefficient is assumed to be constant

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2}$$
(2.7)

When D varies with t, the diffusion is often called *non-Fickian.*[32]

2.5.4   Factors affecting vapor absorption

An understanding of absorption between vapor compounds and polymeric packaging materials requires knowledge of the chemical and physical structures of both the materials.

2.5.4.1   Polymer properties

The properties of a plastic packaging material are the foremost important parameters that control the amount of vapor absorption. The properties of a polymer result from its chemical nature, morphology, formulation (compounding with additives), processing, and even storage and conditions of use. Important parameters derived from the chemical structure, such as glass transition temperature, crystallinity and free volume that have effects on vapor absorption are essentially determined upon the selection of a particular polymer.

Glass transition temperature (Tg)

Figure 2.5 shows the behaviour of one of the many important properties of an amorphous and semicrystalline polymer: the modulus of elasticity.
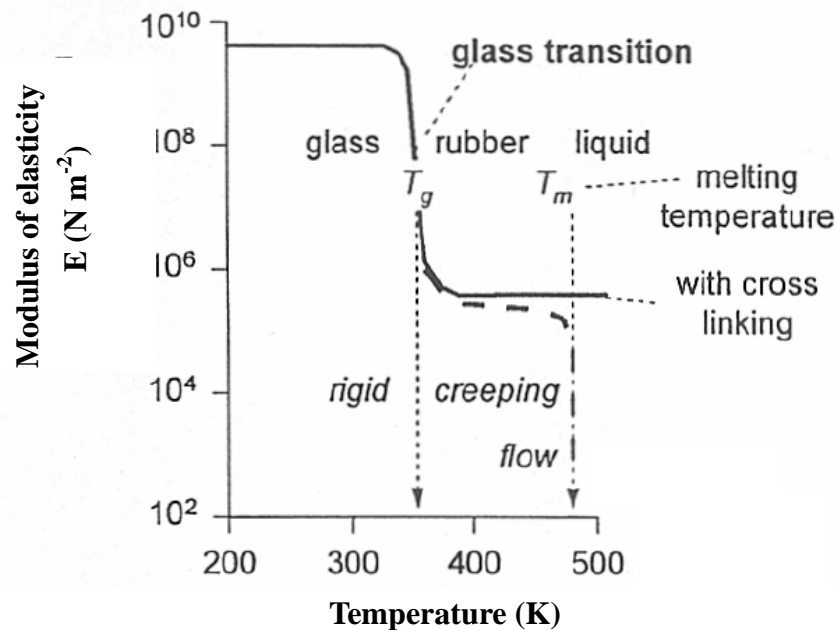
Figure 2.5 Modulus of elasticity against temperature, showing the glass transition and melting temperatures.[33]

There are two sharp breaks indicating phase transitions. At low temperatures the polymer is rigid and brittle: it forms a *'glass'*. At the glass transition temperature Tg the modulus of elasticity drops dramatically. Many of the properties of the polymer change a little at this temperature. Above Tg, the polymer becomes soft and elastic; it forms a *'rubber'*. At high temperatures, the polymer may melt to form a viscous liquid.[30] The polymers that we know as glassy polymers, such as the polyesters, PET, PC and PEN, have T_g, above ambient temperature. At room

temperature, glassy polymers will have very stiff chains and very low diffusion coefficients for vapor molecules at low concentrations. Rubbery polymers such as the polyolefins PE and PP have a T_g below ambient temperature. Rubbery polymers have high diffusion coefficients for vapor compounds and steady-state permeation is established quickly in such structures.[32] Stiff-chained polymers that have a high glass transition temperature generally have low permeability, unless they also have a high free volume.[34]

Free volume

The free volume of a polymer is the molecular 'void' volume that is trapped in the solid state. The permeating molecule finds an easy path in these voids. Generally, a polymer with poor symmetry in the structure, or bulky side chains, will have a high free volume and a high permeability.[35]

Crystallinity

The importance of crystallinity to absorption has been recognized for many years. All polymers are at least partly amorphous: in the amorphous regions the polymer chains show little ordering. However, polymers often contain substantial 'crystalline' parts, where the polymer chains are more or less aligned (Figure 2.6)

Amorphous   Semi-Crystalline

Amorphous
with some space
open, that allows
motion of permeants

Crystalline
(no diffusion)
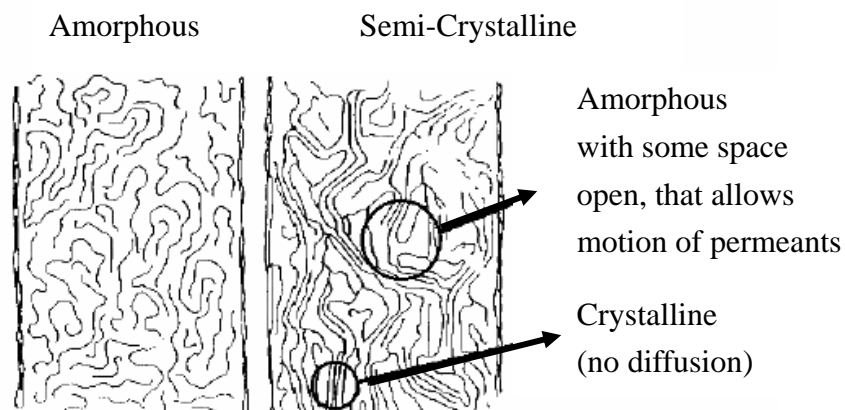
Figure 2.6 An amorphous polymer (left) and a semi-crystalline polymer (right) with amorphous regions (permeable) and crystalline regions (impermeable).[27]

The crystalline areas are a tenth denser than the amorphous parts; for many permeants they are practically impermeable. So, diffusion occurs mainly in the amorphous regions in a polymer, where small vibrational movements occur along the polymer chains. These micro Brownian motions can result in 'hole' formation as parts of the polymer chains move away from each other. It is through such 'holes' that permeant molecules can diffuse through a polymer.[27,33] Therefore, the higher the degree of crystallinity in a polymer, the lower the absorption.

2.5.4.2   Vapor properties of solvent

Concentration

There are relatively few reports relating vapor absorption to the relative concentrations of the sorbants in a liquid or vapor. Mohney *et al.* [36] reported that low sorbant concentrations will only affect the polymer to a very limited extent and the amount of absorbed compounds will be directly proportional to the concentration of the sorbants. At higher concentrations, however, the absorption of compounds into a

polymer material may alter the polymer matrix by swelling.[37,38] Consequently, to avoid overestimation of the amounts of absorbed compounds or swelling of the polymer, it is advisable to use a mixture of compounds in the concentration range that can be expected to be found in a food application.[39] However, to generate reliable and reproducible analytical data, experimental procedures are usually carried out with enhanced concentrations.

Polarity

The polarities of a vapor compound and polymer film are an important factor in the absorption process. The absorption behaviour of different plastic materials has different polarities; hence their affinities toward vapor compounds may differ from each other.[40] Vapor compounds are absorbed more easily in a polymeric film if their polarities are similar.[41] Polyolefins are highly lipophilic and may be inconvenient for packaging products with non-polar substances such as fats, oils, aromas etc., since they can be absorbed and retained by package.[42] The polyesters, however, are more polar than the polyolefins and will therefore show less affinity for non-polar substances.
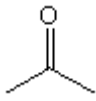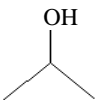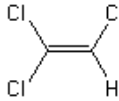
Molecular size and structure

The size of penetrant molecule is another factor. Smaller molecules are absorbed more rapidly and in higher quantities than larger molecules. Very large molecules plasticize the polymer, causing increased absorption into the newly available absorption sites.[43] Generally, the absorption of a series of compounds with the same functional group increases with an increasing number of carbon atoms in the

molecular chain, up to a certain limit. Shimoda *et al.*[44] reported that absorption of aldehydes, alcohols and methyl esters increased with increasing molecular weight up to about 10 carbon atoms. For even larger molecules the effect of molecular size overcomes the effect of the increased solubility of the compounds in the polymer, and the solubility coefficient decreases. Linssen *et al.*[45] reported that compounds with eight or more carbon atoms were absorbed from yoghurt drinks by HDPE, while shorter molecules remained in the product. They also observed that highly branched molecules were absorbed to greater extent than linear molecules.

The properties of the solvents used in this study are included in Table 2.2. According to the vapor pressure property, the solvents can be arranged in order as, acetone, hexane, 1-bromopropane, trichloroethylene and 2-propanol. This property correlates well with the evaporation rate and boiling point of each solvent. The higher evaporation rate and the lower boiling point providing higher vapor pressure of such solvent.

Table 2.2 Physical and chemical properties of organic solvent.[57]

Name	acetone	2-propanol	TCE*	1-bromopropane	n-hexane
Structure					
Classification Category	ketone	alcohol	Chlorinated hydrocarbon	Halogenated hydrocarbon	Aliphatic hydrocarbon
Formular	C_3H_6O	C_3H_8O	C_2HCl_3	C_3H_7Br	C_6H_{14}
Molecular Weight (Daltons)	58.09	60.11	131.38	123	86.2
Boiling Point (^{o}C)	56.07	82.24	86.7	71	68.736
Specific Gravity (25 ^{o}C) (g cm^{-3})	0.78	0.79	1.5	1.353	0.65
Evaporation Rate (BuAc**=1)	5.59	2.5	4.46	4.25	8.9
Vapor Pressure (25°C) (mmHg)	231	45.4	69	138	151.3

* TCE is Trichloroethylene

** BuAC is Butyl acetate

2.5.4.3 External properties

Temperature

Temperature is probably the most important environmental variable affecting transport process. The permeability of gases and liquids in polymers increases with increasing temperature according to the Arrhenius relationship. Possible reasons for increased flavour absorption at higher temperatures are:[40]

• increased mobility of the flavour molecules;

• change in polymer configuration, such as swelling or decrease of crystallinity;

• change in the volatile solubility in the aqueous phase.

Relative humidity

For some polymers, exposure to moisture has a strong influence on their barrier properties. The presence of water vapor often accelerates the diffusion of gases and vapors in polymers with an affinity for water. The water diffuses into the film and acts like a plasticizer. Generally, the plasticizing effect of water on a hydrophilic film, such as ethylene-vinyl alcohol (EVOH) and most polyamides, would increase the permeability by increasing the diffusivity because of the higher mobility acquired by the polymers network.[27] Absorbed water does not affect the permeabilities of polyolefins and a few polymers, such as PET and amorphous nylon, show a slight decrease in the oxygen permeability with increasing humidity. Since humidity is inescapable in many packaging situations, this effect cannot be overlooked. The relative humidity in the environment is often above 50%, and the relative humidity inside a food package can be nearly 100%.[30]

2.6 Literature review on the determination of Volatile Organic Compounds

For the determination of VOCs, several papers have been reported as followed

In 1998, Hodgson *et al.*,[7] studied a dynamic headspace technique for detecting C_6-C_{14} volatile organic compounds (VOCs) in low density polyethylene (LDPE) was discussed in which VOCs were purged with N_2, trapped at ambient temperatures on Tenax-GC, and identified by gas chromatography/mass spectrometry. The results can be used to facilitate a more satifactory isolation and chromatographic identification of VOCs derived from LDPE at ambient temperatures. The isothermal desorption of C_6-C_{14} VOCs from a Tenax-GC sorbent follows first-order kinetics, and

a signification proportion of these compounds is released almost instantaneously (i.e., within a few seconds after the commencement of the desorption process). The results obtained from experiments in which an inert gas is added to the headspace prior to gas transfer to the sample loop confirm that the detector response during dynamic heaspace-GC analysis depends on the total pressure in the sample vial. To maximize the detector response during multiple dynamic headspace-GC analyses, isobaric conditions prior to gas transfer should be maintained and these conditions should be set in such a way that the total pressure in the sample vial is as close as practicable to the static vial pressure.

In 1999, Buchalla *et al.*,[46] reported the investigation of six medical polymers using Thermal Desorption TDS-GC-MS. All polymer: PS, MABS, PA-6, PVC, PE and PP produce detectable amounts of volatiles which remain trapped in the polymer matrix for considerable times, the products and their concentrations are characteristics for each plastic. The main products of PS are acetophenone, benzaldehyde, phenol, 1-phenylethanol, and phenyl acetaldehyde. The same volatiles are observed in Methyl metacrylate-Acrylonitrile-Butadiene-Styrene (MABS), which additionally give some aliphatic compounds. PA-6 yields pentanamide as the main product with traces of some homologous amides. The main product of PVC and PP are fragments of additives, i.e., stabilizers and phenol type antioxidants, respectively. The PE produces only traces of hydrocarbons, aldehydes, ketones, and carboxylic acids, which largely disappear within weeks.

In 2001, Villberg and Veijanen[47] studied a thermal desorption equipment introducing VOCs into the gas chromatographic/mass spectrometric system (GC/MS) with simultaneous sniffing is a suitable method for identifying the volatile organic

off-odor compounds formed during the extrusion coating process of three different plastic materials were collected at two different temperatures (285 and 315 $^{\circ}$C) from an outgoing pipe and near an extruder. The VOCs of fumes were analyzed by drawing a known volume of air through the adsorbent tube filled with a solid adsorbent (Tenax GR). The air samples were analyzed using a special thermal desorption device and GC/MS determination. The simultaneous sniffing was carried out to detect off-odor and to assist in the identification of those compounds that contribute to tainting and smelling. The amounts of off-odor carbonyl compounds and the total content of the VOCs were determined. The most odorous compounds were identified as carboxylic acids while the majority of the volatile compounds were hydrocarbons. The detection and quantification of carboxylic acids were based on the characteristic ion of their mass spectra.

In 2002, Ezquerro *et al*.,[48] studied a method for the identification of VOCs in packaging materials. These compounds are formed by thermooxidative degradation during the extrusion coating process in the manufacture of packaging. Head space solid-phase microextraction was used as a sample preparation technique prior to the determination of VOCs by gas chromatography mass spectrometry. Hydrocarbons and carbonyl compounds such as aldehydes, ketones and carboxylic acids were found in packaging samples obtained by extrusion coating of polyethylene. No compounds with a significant odour were found in the raw materials used in the packaging manufacture. The highest level of carbonyl compound was found in the packaging with an unacceptable odour. Carbonyl compounds, formed from hydrocarbons during the heating of polyethylene, are supposed to be the most propable reason for the organoleptic problems.

Hansen[49] reported cracking of PTFE in kerosene. kerosene has been shown to produce environmental stress cracking in notched PTFE under given load conditions close to its yield strength. Kerosene consists of a large number of different compounds. The component(s) most likely responsible for the failure are those which may not have the highest affinity, judged from similarity of Hansen solubility parameters, but rather those with moderate affinity and lower molecular volumes and molecular cross-sections. Those compounds with highest similarity have relatively large molecular volumes and minimum molecular cross-sections, since they can be expected to be those with some degree of cyclic structure. This will present rapid entry or perhaps prevent entry altogether into the PTFE. Whatever the nature of the harmful absorption, presumed significant amounts could not be found by weight gain measurements within reasonable times. This could indirectly suggest a failure initiated at or very near the PTFE surface by liquids having high affinity, but little ability to absorb. On the other hand, absorption is most likely by the smaller and more linear molecular species. These can absorb slightly even though their affinities may not be the highest in the multicomponent kerosene.

In 2003, Ezquerro *et al*.,[50] studied the quantification of VOCs in flexible multilayer packaging materials using headspace solid-phase microextraction-gas chromatography-mass spectrometry. Hexadecane is a solvent valid for the preparation of standards and the quantification of VOCs. The analytes include 22 compounds such as aldehydes, ketones, carboxylic acids and hydrocarbons formed by thermooxidative degradation of polyethylene during the extrusion coating process in the manufacture of the packaging, and many of them are involved in the unpleasant and undesirable odour of these materials. The influence of the extraction time on the amount extracted

was studied for a standard solution of the analytes in hexadecane, together with the influence of the volume of the standard solution and the amount of the sample placed in the vial. HS-SPME is a technique that simplifies the quantitative analysis of VOCs in solid samples and avoids the use of organic solvents to prepare the samples.

Ezrin and Lavigne[51] reported the analysis of aromatic hydrocarbons in plastic packaging materials of polyethylene, polystyrene, poly(vinyl chloride) and poly(ethylene terephthalate) using thermal desorption gas chromatography/mass spectrometry. All four types contain detectable levels of benzene, toluene, xylenes and naphthalene compounds.

In 2004, Wo *et al*.,[52] studied the investigation of VOCs in the air of class-100 cleanrooms at liquid crystal display (LCD) fabrication facilities. Air samples were collected on multisorbent tubes (including Carbopack B, Carbopack C, and Carbosieve S-III) and analyzed using adsorption/thermal desorption coupled with gas chromatography-mass spectrometry (GC-MS). The method appears to be accurate, sensitive, simple and well-suited for determining VOC distributions from various stages of LCD manufacturing process and temporal variations of the analyte concentrations. The thermal desorption method using multisorbent tubes including Carbopack B, Carbopack C, and Carbosieve S-III) has been successfully applied to the analysis of VOCs in workplace air.

In 2005, Limam *et al*.,[53] studied the sorption of organic solvents (1-butanol and 1-octanol) by poly(ethylene terephthalate) and TOPAS® (cyclic olefin copolymers or COC) was investigated at 3,23 and $42^{o}C$ by coupling two techniques (in an off-line way) : supercritical fluid extraction to GC/MS. Highly crystalline polymers show lower sorption of organic solvents than amorphous polymers. Among the parameters

which affect the process of retention of these solvents, the interaction of solvent-polymer structure stands out as the most important, but it is necessary to consider the influence of other external parameters such as the immersion time, the temperature, the film thickness, and etc. Therefore, the diffusions of 1-butanol are less important in PET than in TOPAS® (completely amorphous).

CHAPTER III

EXPERIMENTAL

3.1 Instruments

Gas Chromatograph Mass spectrometry (GC-MS) : Agilent Technologies model HP6890N/5973, Shanghai, China.

Thermal Desorption Unit : Markes international Ltd., model TDU, Pontyclun, UK.

Scanning Electron Microscope (SEM) : JEOL, model JSM5310LV, Tokyo, Japan.

Fourier Transform Infrared Spectrometer (FTIR) : Perkin Elmer, model Spectrum 100 / spotlight 400, Bucks, UK.

Thermogravimetric and Differential Thermal Analysis (TG/DTA) : Seiko Instrument, model TG/DTA 220, Tokyo, Japan.

3.2 Chemicals

n-hexane, AR grade, Merck, Darmstadt, Germany.

2-propanol, AR grade, Merck, Darmstadt, Germany.

Acetone, AR grade, Merck, Darmstadt, Germany.

Ttrichloroethylene, AR grade, Merck, Darmstadt, Germany.

1-bromopropane, AR grade Dipsol chemicals Co.,Ltd., Tokyo, Japan.

Hexadecane, Spectroscopy grade, Merck, Darmstadt, Germany.

Dichloromethane, Spectroscopy grade, Merck, Darmstadt, Germany.

Carbotrap B, Markes international Ltd., Pontyclun, UK.

Carbotrap C, Markes international Ltd., Pontyclun, UK.

Tenax TA, Markes international Ltd., Pontyclun, UK.

Carbograph-1, Markes international Ltd., Pontyclun, UK.

Polypropylene packaging, Salee Industry Co., Ltd., Bangkok, Thailand. The polypropylene homo-polymer (isotactic type) was supplied by Titan PP Polymers (M) Sdn. Bhd.

Poly(ethylene terephthalate) packaging, Salee Industry Co., Ltd., Bangkok, Thailand. The poly(ethylene terephthalate) was supplied by Thai Shinkong Industry Corporation Ltd.

Table 3.1 shows some of the characteristics of the polymers used in this thesis.

Table 3.1 Characteristics of the polymers.[a]

Polymer	Mw (g mol^{-1})	Polarity	T_g[b](°C)	T_m[c](°C)	Crystallinity (%)	Density (g cm^{-3})
PP	37500	Apolar	-5 to 0	165 $\pm$ 5	43	0.9
PET	52000	Polar	+80	244 $\pm$ 4	57	1.2

[a] Specifications from manufacturers

[b] Glass transition temperature

[c] Melting temperature

The additives used in plastics are summarized in Table 3.2.

Table 3.2 Additives used in plastics (PP and PET).[d]

Additive	Plastic	
	PP	PET
Nucleating agent	0.1-0.3 % wt Salt of phthalic acid	-
Lubricant	0.2-0.3 % wt Paraffin wax	-
Antistatic agent	-	0.1-0.2 % wt Ethoxylated fatty alkylamines
Antioxidant	0.05-0.3% wt Phenols	0.05-0.3% wt Dialkyl hydroxylamines

[d] Specifications from manufacturers

3.3   Preparation of standard solution for GC-MS

Preparation of the stock solution

A 10 µg/µL solution was prepared by weighing 0.25 $\pm$ 0.005 g of hexadecane standard into an empty vial. Then the material was rinsed out of the vial by dichloromethane and it was transferred to 25 mL volumetric flask.

The rinsing was repeated until the volume was nearly 25 mL. The final volume of volumetric flask was carefully adjusted by a syringe or a dropper.

Preparation of 200 ng/µL solution

The stock solution of 200 µL was transferred into a 10 mL volumetric flask, the final volume was adjusted to 10 mL by a syringe or a dropper. For the analysis, the concentration of 1,000 ng was prepared by injecting 5 µL of 200 ng µL^{-1}

concentration of the standard solution.

3.4 The analysis of VOCs in packaging materials

Each sample of poly(ethylene terephthalate) and polypropylene was cut into pieces of 1.5 cm x 4 cm size. The analysis of VOCs in the sample was investigated and was identified by Thermal Desorption-Gas Chromatography-Mass Spectrometry.

3.5 The analysis of organic vapor absorption in packing material

Polypropylene and poly(ethylene terepthalate) packaging material were cut into pieces of 1.5 cm x 4 cm size. Each sheet was kept in an organic vapor condition by hanging the samples in a 100 mL glass jar filled with 20 mL solvent. The absorption times were varied from 1 to 30 days. The absorption of the sample was investigated and was identified by Thermal Desorption-Gas Chromatography-Mass Spectrometry.

3.6 Thermal Desorption-Gas Chromatography-Mass Spectrometry analysis

3.6.1 Sampling procedure

The sample to be analyzed was placed in a sample chamber and attached at its top. The sample-containing chamber was placed in a the laboratory oven in which the incoming gas lines were attached leading to the adsorbent tubes. The adsorbent tubes were custom-made of stainless steel. They were packed with solid adsorbents (100 mg Carbotrap B and 200 mg Carbotrap C), silanized glass wool plugs were used to hold the adsorbents and also plugged at the ends with the same material. Before sampling, all tubes were conditioned at 350 $^{\circ}$C for more than 10 min and tested before use. The blank chromatograms were obtained under the same conditions of analysis

and at the maximum sensitivity confirmed that no peak of impurity presence which could disturb the gas chromatographic analysis. The rate of gas nitrogen flow was 50 $\pm$ 2 mL min^{-1}. The samples were allowed for three hours at 85°C (The tested temperature was performed at 85°C which is resemble the temperature of HDD while it is working). The adsorbent tube was removed from the line and placed into a thermal desorption Unit.

3.6.2 Chromatographic conditions

The GC-MS system was equipped with an XTI-5 column (30 m x 0.25 mm x 0.25 µm). An initial oven temperature of 40°C for 2 min was used, followed by an increase temperature at a rate of 12°C min^{-1} to 280°C and to a final hold at 280°C for 20 min. The flow rate of carrier gas helium was 2 mL min^{-1}. The injector was maintained at 280°C with a 15:1 split ratio. The mass spectrometer was scanned from the m/z 33 to 550 at a cycle of 1 s, the fragmentation was made by electronic impact, and the ion trap temperature was 200 ^{o}C. The GC and MS conditions are listed in Table 3.3.

Table 3.3 GC-MS parameter for the analysis of VOCs (GC-MS, Agilent

Technologies, model HP6890N/5973, Shanghai, China).

GC/MC conditions	Specification
Column type	XTI-5 (30.0 m x 0.25 mm x 0.25 um)
Column flow	1 mL min
Carrier gas	Helium (purity 99.999%)
Inlet system	Split 50:1
GC Condition	
Injector temperature	250^oC
Oven program	
Initial temperature	40^oC
Initial time	2 min
Ramp	12^oC min^{-1}
Final temperature	280^oC
Final time	20 min
Interface temperature	280^oC
MS Condition	
Mass range	33-550
Threshold	150
Scan	2.85 scans s^{-1}

3.6.3   Thermal Desorption Unit

A special thermal desoption unit was used to introduce the samples into the

GC-MS system. The UNITY is a thermal desorption system developed for the

introduction of samples into GC-MS system.

3.6.3.1 Sample tubes

UNITY is compatible with industry standard sample tubes, 3.5 inches (89 mm) long by 1/4 inch (6.4 mm) O.D with 5 mm (stainless steel and coated steel) or 4 mm (glass) I.D.. The sorbent was the retained in stainless steel (or coated steel) tubes with stainless steel (or coated steel) gauzes and gauze retaining spring. Glass wool was for retaining the sorbent in the glass tubes.

3.6.3.2 Tube desorption oven

The UNITY tube desorption oven heated up rapidly ($\sim150^{o}C$ min^{-1}) at the start of elevated temperature purge or tube desorption. It began to cool at the end of primary (tube) desorption and reached $50^{o}C$ from $300^{o}C$ within 10 min.

3.6.3.3 Tube filters and seals

When it was ready for the analysis, the sample tubes was placed into the cool desorption oven with the sampling (grooved) end pointing to the rear of the instrument. Operation of the lever mechanism seals the sample tube into the UNITY flow path. Temperature resistant Viton O-rings were sealed onto the outer wall of the sample tube, ~2 mm for either end. A porous PTFE filter sat just behind the O-ring in both sample tube seals. These prevented the UNITY flow path from contamination in the event that sorbent particles or high boiling sample materials migrated out of the tube.

3.6.3.4 The cold trap

The cold trap contains a 2 mm diameter x 60 mm long bed of sorbent supported by glass wool.

3.6.3.5 Cold trap cooling and heating

UNITY contains a 2-stage peltier cell, which uniformly cools the entire 60-mm sorbent bed to a minimum temperature of -10 $^{\circ}$C in ambient temperatures as high as +30 $^{\circ}$C. At -10 $^{\circ}$C, a cold trap packed with an appropriate series of sorbents including carbonised molecular sieve, allowed a quantitative retention of compounds such as ethane and freons from over 500 ml of gas/air. No liquid cryogen was required. With the trap at -15 $^{\circ}$C the quantitative recovery of ethylene could demonstrated from over 200 ml of gas/air. Once all the target analytes had been collected and focused in the cold trap, the trap oven heated ballistically with the reaching rates in excess of 60 $^{\circ}$C sec^{-1} for the first critical stages of trap desorption. Uncompromised capillary chromatography was produced without on-column focusing but with a desorption flow as low as 2 ml min^{-1}. This facilitates a splitless operation with high-resolution capillary GC.

3.6.3.6 Gas flow through the cold trap

The UNITY cold trap operates in a backflush mode, i.e., the sample gas stream enters and leaves the cold trap through the narrow-bore/restricted end which points to the rear of the instrument. The backflush desorption allows use of a series of 2 or 3 sorbents of increasing strength in the cold trap – Tenax TA (weak) backed up by Carbograph 1 (medium). This facilitates the analysis of wide volatility range samples.

High boiling compounds were retained and quantitatively desorbed from the first weak sorbent, without ever coming into contact with the stronger sorbents behind.

3.6.3.7 Trap filters and seals

As with the sample tube, the cold trap was sealed into the gas flow path of UNITY via O-rings, which sealed on the outer wall of the trap tube. At the cool non-valve end of the trap, the O-ring was backed up with a porous PTFE filter to prevent contamination of the pneumatics in the event of sorbent particles migrating out of the trap.

The thermal desorption parameter are listed in Table 3.4.

Table 3.4 Thermal desorption parameter for the analysis of VOCs.

Parameter	Value
Thermal-extraction temperature	$250^{o}C$
Desorption time	10 min
Desorption for the trap at low temperature	$-10^{o}C$
Desorption for the trap at high temperature	$320^{o}C$
Desorption for the trap heating rate	$12^{o}C\ sec^{-1}$
Temperature of transfer line	$200^{o}C$
Primary adsorbent for sample tube	100 mg carbotrap B + 200 mg carbotrap C
Secondary adsorbent for sample tube	Tenax TA + Carbograph-1

3.6.3.8 Quantitative Measurements

Quantification was performed by using an external standard. Aliquots of 5 µL of 200 ng µL^{-1} of hexadecane were injected into the adsorbent tubes and analyzed under the same conditions as the samples. After the MS run, the detected peak areas of all compounds were observed and compared with peaks of the standard.

3.7   Scanning Electron Microscope (SEM)

In the high vacuum chamber, the electron beam the generated from the tungsten filament was incident to the specimen surface. The SEM image was produced from the secondary electron and back scattering electron. The JSM-5310 scanning microscope was used for the observation of surfaces of the samples at a magnification of 1000X.

3.8   Fourier Transform Infrared Spectroscopy (FTIR)

Infrared spectroscopy was performed with a Perkins Elmer (model Spectrum 100) instrument, with a resolution 4 cm^{-1}, number of scan was 16 scans, in the range of 4000-700 cm^{-1}. The samples were directly analyzed by FTIR microscopy in a transmittance mode in order to investigate organic vapor absorption on plastic packaging materials.

3.9   Characterization of the samples by TG/DTA

The Thermogravimetric and Differential Thermal Analysis (TG/DTA 220) interfaced to a PC was used to determine T_m of poly(ethylene terephthalate) and polypropylene. The samples were cut from sheets using a weight between 5-10 mg.

An empty aluminum pan was used as reference. The samples were heated from 30 to 300°C at a rate of 10°C min^{-1}.

3.10   Dimension Measurement

The thickness of sample was measured using a vernier. Each sample was performed in triplicate and the average of these measurements was repeated as thickness value of the specimens.

CHAPTER IV

RESULTS AND DISCUSSION

In this research, the detection of hydrocarbons compounds and total VOCs in polypropylene and poly(ethylene terephthalate) plastic using Thermal desorption by Gas Chromatography-Mass Spectrometry (GC-MS) was explored. Fourier transform infrared spectrometer (FTIR) was used for the characterization of materials providing information on the molecular structure of plastic packaging materials. Scanning electron microscope (SEM) was used to observe the surface condition of plastic packaging material. Thermogravimetric and differential thermal analysis (TG-DTA) was used for the characterization of thermal property of materials. However, the appropriate of packaging material can be used as a protecting aid of contamination and may help solving many cleanliness issues.

4.1   The analysis of VOCs in the packaging material

The analysis of VOCs present in packaging is important to control the cleanliness of product. The use of thermal desorption trapping to concentrate VOCs prior to the analysis has been established as a proven technique for VOCs analysis, this method involves collecting the sample.[54] After the collection, the trap was rapidly heated, the VOCs were desorbed, and typically the compounds were analyzed using a gas chromatographic system. The preceeding analysis gave an means for the identification of the compounds from a mixture. This may be possible by several means, such as condensation for exploiting the substantial difference in boiling points absorption for exploiting the solubility in different solvents or adsorption for exploiting the adsorptivity on different adsorbents.[55]

The amount in nanogram of each compound was calculated based on the peak area of hexadecane as an internal standard. Each analysis was performed in triplicate for reproducibility assurance.

4.1.1 The analysis of hydrocarbon and total VOCs from polypropylene and poly(ethylene terephthalate)

Hydrocarbon and total VOCs on polypropylene and poly(ethylene terephthalate) were analyzed using thermal desorption technique in Gas Chromatography-Mass Spectrometry (GC-MS). Then the results were compared between polypropylene and poly(ethylene terephthalate).

Fig. 4.1 shows hydrocarbon amounts which were released from polypropylene (PP) and poly(ethylene terephthalate) (PET). The total amounts of VOCs from polypropylene and poly(ethylene terephthalate) were 6024 ng cm^{-2} and 226 ng cm^{-2}, respectively. The hydrocarbon amounts from polypropylene and poly(ethylene terephthalate) were 4550 ng cm^{-2} and 205 ng cm^{-2}, respectively. The main compounds detected from polypropylene and poly(ethylene terephthalate) are hydrocarbon compound. From the analysis data, poly(ethylene terephthalate) contains much less hydrocarbon and total VOCs than those from polypropylene. This is probably due to the residual monomer/oligomers of polypropylene.

The VOCs in packaging materials are mostly produced by thermooxidative degradation of polyolefins and polyesters in the extrusion coating process. This process is necessary to achieve good adhesion properties, and entails depositing melting polymers on solid surfaces. The combination of high temperatures, often extreme shear stress and the presence of oxygen leads to the formation of organic

radicals, and the combination of these radicals produces oxygenated compounds.
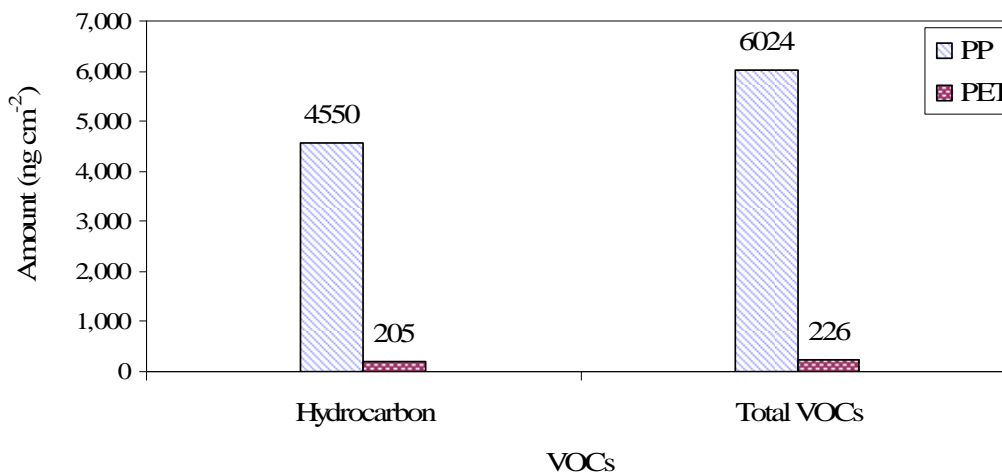
Fig. 4.1 Hydrocarbon and total VOCs in polypropylene and poly(ethylene terephthalate).

4.1.2 The analysis of VOCs in polypropylene and poly(ethylene terephthalate)

The identification of VOCs in polypropylene and poly(ethylene terephthalate) packaging materials is presented in this study using thermal desorption technique of Gas Chromatography-Mass Spectrometry (GC-MS). Then the results were compared between polypropylene and poly(ethylene terephthalate).

Fig. 4.2 shows the identification of VOCs which were released from polypropylene and poly(ethylene terephthalate). The main compound was detected from polypropylene are hydrocarbon as shown in Fig. 4.1. Other compounds are ester, naphthalene, benzene derivatives, aldehyde, ketone, phenol and carboxylic acid. The phenol and carboxylic acid are fragment of additives, antioxidant and nucleating agent, respectively. Also the main compound was detected from poly(ethylene terephthalate)

are hydrocarbon. Other compounds are alcohol, aldehyde, ester and amine. The amines are fragment of additives, antistatic agent and antioxidant. The similar causes as those of section 4.1.1 are applied to this case. The mechanism of thermooxidative degradation highlights the presence of alkyl radicals that combined with oxygen alkoxy and peroxy radical and the combinations of these radicals produces VOCs as hydrocarbon, ester, naphthalene, benzene derivatives, aldehyde, ketone, alcohol, phenol and carboxylic acid.

From the result, poly(ethylene terephthalate) contains much less of each VOCs than polypropylene as shown in Fig. 4.2. A few VOCs in poly(ethylene terephthalate) was detected but many VOCs in polypropylene were found. The low level of VOCs in poly(ethylene terephthalate) packaging material should be used as a protecting aid of contamination and may help solving many cleanliness issue.
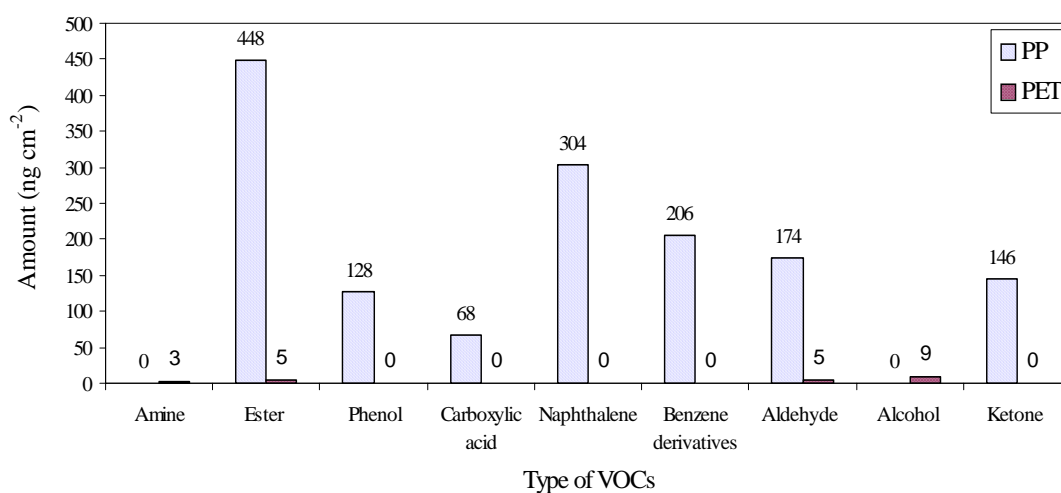
Fig. 4.2 The identification of VOCs from polypropylene and poly(ethylene terephthalate).

4.2   Effect of organic vapor on VOCs in packaging material

4.2.1 Effect of organic vapor on VOCs in polypropylene packaging material

The effects of organic vapor on VOCs in polypropylene were investigated by thermal desorption via Gas Chromatography-Mass Spectrometry. The absorption time was varied from 1, 3, 7, 15 and 30 days. Tables 4.1 – 4.5 present the effect of organic vapor on VOCs in polypropylene packaging material. Hydrocarbon and total VOCs were obviously increased from the packaging material without the added organic vapors in the chamber. The high amount of hydrocarbon may be caused by the residual monomer/oligomers of polypropylene packaging, which gave a higher amount of total VOCs. It was observed that the esters, naphthalenes, benzene derivatives, aldehydes, ketones, phenols and carboxylic acids were all detected in both polypropylene under organic vapor exposure. The organic vapor affects VOCs in PP, such as a slight increase in esters due to lower stability of such functional groups. Moreover, diffusion of gas in the chamber depends on vapor pressure, miscibility, and thermal conductivity of gas which is temperature dependence. Therefore, gas with high vapor pressure and good miscibility tends to permeate better into the plastic. Besides these factors, the permeability of gas diffused out of the plastic also depends on morphology, % crystallinity, melting temperature, molecular weight of the plastic and the testing temperature.

Table 4.1 Effect of acetone vapor on VOCs in polypropylene packaging material.

Compound	The amount of VOCs (ng cm^{-2}) obtained for exposure time (days)					
	1*	1**	3**	7**	15**	30**
Acetone	0	98	119	140	155	152
Hydrocarbons	4371	7575	7745	7879	7997	8201
Esters	400	451	461	456	449	460
Phenol	140	132	134	124	124	132
Carboxylic acid	60	101	79	89	92	95
Naphthalene	320	279	281	299	298	288
Benzene derivatives	210	211	220	204	211	235
Aldehydes	150	156	177	183	176	180
Ketones	170	176	170	157	169	177
Total VOCs	5821	9178	9386	9530	9672	9919

* in the presence of air

** in the presence of air and the specific organic vapor

Table 4.2 Effect of 1-bromopropane vapor on VOCs in polypropylene packaging

material.

Compound	The amount of VOCs (ng cm^{-2}) obtained for exposure time (days)					
	1*	1**	3**	7**	15**	30**
1-bromopropane	0	129	173	195	255	251
Hydrocarbons	4371	5995	6032	6245	6432	6551
Esters	400	441	444	436	431	441
Phenol	140	123	127	132	124	130
Carboxylic acid	60	61	63	60	62	63
Naphthalene	320	235	230	278	281	287
Benzene derivatives	210	195	188	180	211	220
Aldehydes	150	144	153	150	151	181
Ketones	170	157	150	169	170	169
Total VOCs	5821	7479	7561	7845	8118	8292

* in the presence of air

** in the presence of air and the specific organic vapor

Table 4.3 Effect of hexane vapor on VOCs in polypropylene packaging material.

Compound	The amount of VOCs (ng cm^{-2}) obtained for exposure time (days)					
	1*	1**	3**	7**	15**	30**
hexane	0	331	450	597	679	671
Hydrocarbons	4371	6014	6124	6245	6344	6545
Esters	400	450	479	484	481	478
Phenol	140	98	124	111	121	113
Carboxylic acid	60	61	62	62	64	62
Naphthalene	320	226	229	221	231	234
Benzene derivatives	210	158	148	151	168	170
Aldehydes	150	134	132	133	140	136
Ketones	170	144	140	146	145	140
Total VOCs	5821	7616	7888	8150	8373	8549

* in the presence of air

** in the presence of air and the specific organic vapor

Table 4.4 Effect of 2-propanol vapor on VOCs[a] in polypropylene packaging material.

Compound	The amount of VOCs (ng cm^{-2}) obtained for exposure time (days)					
	1*	1**	3**	7**	15**	30**
2-propanol	0	90	122	136	148	142
Hydrocarbons	4371	5546	5740	5975	6067	6206
Esters	400	451	451	471	461	461
Phenol	140	160	171	181	131	126
Carboxylic acid	60	71	61	66	80	70
Naphthalene	320	281	291	321	331	310
Benzene derivatives	210	146	156	161	178	151
Aldehydes	150	201	191	196	200	190
Ketones	170	151	161	161	177	165
Total VOCs	5821	7096	7342	7666	7772	7821

* in the presence of air

** in the presence of air and the specific organic vapor

Table 4.5 Effect of trichloroethylene vapor on VOCs in polypropylene packaging material.

Compound	The amount of VOCs (ng cm^{-2}) obtained for exposure time (days)					
	1*	1**	3**	7**	15**	30**
trichloroethylene	0	111	124	141	175	158
Hydrocarbons	4371	6335	6578	6723	6799	6951
Esters	400	404	420	436	431	441
Phenol	140	132	141	157	161	156
Carboxylic acid	60	58	61	60	66	60
Naphthalene	320	276	291	286	291	271
Benzene derivatives	210	257	271	281	291	276
Aldehydes	150	155	161	171	181	176
Ketones	170	150	146	150	145	151
Total VOCs	5821	7879	8191	8404	8539	8638

* in the presence of air

** in the presence of air and the specific organic vapor

4.2.2   Effect of organic vapor on VOCs in poly(ethylene terephthalate) packaging material

The effects of organic vapor on VOCs in poly(ethylene terephthalate) were investigated by thermal desorption via Gas Chromatography-Mass Spectrometry. The absorption times were varied from 1, 3, 7, 15 and 30 days. Tables 4.6 – 4.10 present the effect of organic vapor on VOCs in poly(ethylene terephthalate) packaging material. The main compound was detected from poly(ethylene terephthalate) as hydrocarbon which was not much different in the amount when organic vapor absorption time reached 30 days. It was observed that total VOCs released from poly(ethylene terephthalate) was slightly increased until the absorption time was 30 days but it was not much in the amount of total VOCs. Besides the mentioned VOCs, naphthalene and benzene derivatives were additionally detected in the packaging materials. It was observed that ester compound was obviously increased from the packaging material without the added organic vapors in the chamber but not much was found in the amount of ester when the absorption time reached 30 days. The naphthalene and benzene derivatives and a high amount of the ester may be caused by the residual monomer/oligomers of poly(ethylene terephthalate). Moreover, the organic vapor affects other VOCs in poly(ethylene terephthalate), such as a slight increase in alcohol and aldehyde.

Table 4.6 Effect of acetone vapor on VOCs in poly(ethylene terephthalate)

packaging material.

Compound	The amount of VOCs (ng cm^{-2}) obtained for exposure time (days)					
	1*	1**	3**	7**	15**	30**
Acetone	0	33	45	55	69	66
Hydrocarbons	190	204	215	211	234	253
Esters	13	115	110	118	120	121
Alcohols	5	10	12	10	12	11
Amines	3	5	5	4	4	4
Naphthalene	0	10	13	14	15	14
Benzene derivatives	0	5	5	6	6	8
Aldehydes	2	5	4	5	5	4
Total VOCs	213	385	410	424	465	480

* in the presence of air

** in the presence of air and the specific organic vapor

Table 4.7 Effect of 1-bromopropane vapor on VOCs in poly(ethylene terephthalate)

packaging material.

Compound	The amount of VOCs (ng cm^{-2}) obtained for exposure time (days)					
	1*	1**	3**	7**	15**	30**
1-bromopropane	0	25	39	53	56	45
Hydrocarbons	190	210	212	215	216	211
Esters	13	65	65	71	57	61
Alcohols	5	9	12	14	11	10
Amines	3	4	4	6	5	4
Naphthalene	0	10	13	14	13	13
Benzene derivatives	0	6	5	3	6	5
Aldehydes	2	13	11	11	10	7
Total VOCs	213	342	362	387	372	356

* in the presence of air

** in the presence of air and the specific organic vapor

Table 4.8 Effect of hexane vapor on VOCs in poly(ethylene terephthalate)

packaging material.

Compound	The amount of VOCs (ng cm^{-2}) obtained for exposure time (days)					
	1*	1**	3**	7**	15**	30**
hexane	0	23	29	38	49	36
Hydrocarbons	190	191	211	210	211	210
Esters	13	53	58	56	54	58
Alcohols	5	9	10	9	11	10
Amines	3	13	13	15	14	10
Naphthalene	0	12	12	13	12	13
Benzene derivatives	0	5	6	6	4	6
Aldehydes	2	3	4	5	6	5
Total VOCs	213	310	342	352	360	347

* in the presence of air

** in the presence of air and the specific organic vapor

Table 4.9 Effect of 2-propanol vapor on VOCs in poly(ethylene terephthalate)

packaging material.

Compound	The amount of VOCs (ng cm^{-2}) obtained for exposure time (days)					
	1*	1**	3**	7**	15**	30**
2-propanol	0	28	38	51	63	53
Hydrocarbons	190	173	212	199	203	220
Esters	13	81	76	80	79	80
Alcohols	5	11	14	12	13	12
Amines	3	7	5	7	7	6
Naphthalene	0	10	10	12	11	12
Benzene derivatives	0	5	4	6	6	3
Aldehydes	2	2	6	5	5	4
Total VOCs	213	318	365	372	388	391

* in the presence of air

** in the presence of air and the specific organic vapor

Table 4.10 Effect of trichloroethylene vapor on VOCs in poly(ethylene terephthalate) packaging material.

Compound	The amount of VOCs (ng cm^{-2}) obtained for exposure time (days)					
	1*	1**	3**	7**	15**	30**
trichloroethylene	0	26	38	57	60	48
Hydrocarbons	190	213	226	200	203	211
Esters	13	61	60	63	65	65
Alcohols	5	9	8	9	8	10
Amines	3	4	4	5	4	5
Naphthalene	0	10	12	12	11	12
Benzene derivatives	0	6	6	6	6	6
Aldehydes	2	7	7	8	7	8
Total VOCs	213	335	361	361	364	365

* in the presence of air

** in the presence of air and the specific organic vapor

4.3   The analysis of organic vapor absorption in packaging material

The analysis of organic vapor absorption present in packaging material is important to control the cleanliness of product. The use of thermal desorption trapping to concentrate organic vapor prior to the analysis has been established as a proven technique for organic vapor analysis, this method involves collecting the sample. After collection, the trap is rapidly heated, the organic vapor are desorbed, and typically the compounds are analyzed using a gas chromatographic system. The preceeding analysis gave an indication of the identification of the compounds from a mixture. This may be possible by several means, such as condensation (exploiting the substantial difference in boiling points), absorption (exploiting the solubility in different solvents) or adsorption (exploiting the adsorptivity on different adsorbents).[55]

The amount in the nanogram scale of each compound was calculated based on the peak area of hexadecane as an internal standard. Each analysis was performed in triplicate for reproducibility assurance.

4.3.1 The analysis of organic vapor absorption in polypropylene packaging materials

Table 4.11 presents the analysis result of organic vapor absorption in polypropylene packaging material. It was observed that the amount of organic released from polypropylene packaging materials was increased when the absorption time reached 15 days and then the amount of organic vapor absorption was decreased when the absorption time was 30 days.

Table 4.11 Organic vapor absorption in polypropylene packaging material.

Organic vapor	Acetone amount (ng cm^{-2})/ Absorption time (days)				
	1	3	7	15	30
acetone	98	119	140	155	152
1-bromopropane	129	173	195	255	251
hexane	331	450	597	679	671
2-propanol	90	122	136	148	142
trichloroethylene	111	124	141	175	158

The organic vapor absorptions in polypropylene from highest to lowest can be ranked as follows: n-hexane, 1-bromopropane, trichloroethylene, acetone and 2-propanol. As a rule of thumb, a solvent having a solubility parameter close to that of a polymer, its vapor absorption in polymer is thus high.

4.3.2 The analysis of organic vapor absorption in poly(ethylene terephthalate) packaging materials

Table 4.12 presents the analysis result of organic vapor absorption in poly(ethylene terephthalate) packaging material. It was observed that the amount of organic released from poly(ethylene terephthalate) packaging materials was increased when the absorption time reached 15 days. However, the amount of organic vapor absorption was decreased when the absorption time was 30 days.

Table 4.12 Organic vapor absorption in polypropylene packaging material.

Organic vapor	Acetone amount (ng cm^{-2})/ Absorption time (days)				
	1	3	7	15	30
acetone	33	45	55	69	66
1-bromopropane	25	39	53	56	45
hexane	23	29	38	49	36
2-propanol	28	38	51	63	53
trichloroethylene	26	38	57	60	48

The organic vapor absorptions in poly(ethylene terephthalate) can be ranked from highest to lowest as follows: acetone, 2-propanol, trichloroethylene, 1-bromopropane and n-hexane. As a rule of thumb, a solvent having a solubility parameter close to that of a polymer, its vapor absorption in polymer is thus high.

Table 4.13 presents vapor pressure of the solvents and relationship between solubility parameters of organic solvents and plastics (PP and PET). As described in section 4.3.1 and section 4.3.2, a solvent having a solubility parameter close to that of a polymer, its vapor absorption in polymer is thus high. The polypropylene and poly(ethylene terephthalate) show the highest hexane vapor absorption and acetone vapor absorption, respectively. These results correlates well with the high vapor pressure of hexane and acetone. Additionally, the dispersive component of solubility parameter of hexane is close to that of PP, suggesting compatibility between solvent and plastic. The rest of solvents are in the order of 1-bromopropane, trichloroethylene, acetone and 2-propanol according to the order their dispersive components. Whereas,

acetone and 2-propanol show the most compatibility with PET due to the closest polarity and hydrogen bonding components of solubility parameter. Other solvents, trichloroethylene, 1-bromopropane, and hexane are less compatible due to smaller polarity effect, which is none in case of hexane.

Table 4.13 Vapor pressure of the solvents and relationship between solubility parameters of organic solvent and plastics (PP and PET).

Solvent	Vapor pressure (25 ^{o}C) (mmHg)	Solubility parameter (MPa)$^{1/2}$				$\|\delta_{solvent} - \delta_{plastic}\|$	
		δ_D	δ_P	δ_H	Total δ	PP	PET
Acetone	231	15.5	10.4	7.0	19.7	3.94	1.80
1-bromopropane	138	16.4	7.9	4.8	18.2	2.44	3.30
Hexane	151.3	14.9	0	0	14.9	0.86	6.60
2-propanol	45.4	15.8	6.1	16.4	23.5	7.74	2.00
Trichloroethylene	69	18	3.1	5.3	18.7	2.94	2.80
PP	-	15.76	0	0	15.76	-	-
PET	-	19.44	3.48	8.59	21.5	-	-

PP $\delta_T = 15.76$ (MPa)$^{1/2}$

PET $\delta_T = 21.5$ (MPa)$^{1/2}$

Fig. 4.3 shows the organic vapor absorption in polypropylene and poly(ethylene terephthalate) packaging material. From the results, all those of organic vapor absorptions in poly(ethylene terephthalate) are less than polypropylene. At room temperature, poly(ethylene terephthalate) has very stiff chains with very low diffusion for vapor. Polypropylene has high diffusion for vapor and steady-state permeation can be established quickly in such a structure. Beside the solubility parameter and vapor effects mentioned earlier, it was also observed that the phenomenon of vapor sorption depends on the following parameters.

1. characteristics of the polymer: molecular weight, degree of crystallinity, glass transition temperature (T_g)

2. absorption time

According to the results, the organic vapor absorption of each solvent in the polypropylene are much higher than those obtained in the poly(ethylene terephthalate). This can be explained from the molecular weight, crystallinity, and T_g differences between polypropylene and poly(ethylene terephthalate). The polypropylene shows a lower molecular weight, crystallinity, and T_g than the poly(ethylene terephthalate). Thus, polymers considered as being a barrier against solvent diffusion are those with a high ratio of crystallinity. Therefore, the flexible chains and amorphous structure present in PP allow solvent vapor to penetrate more than the rigid structure of PET.
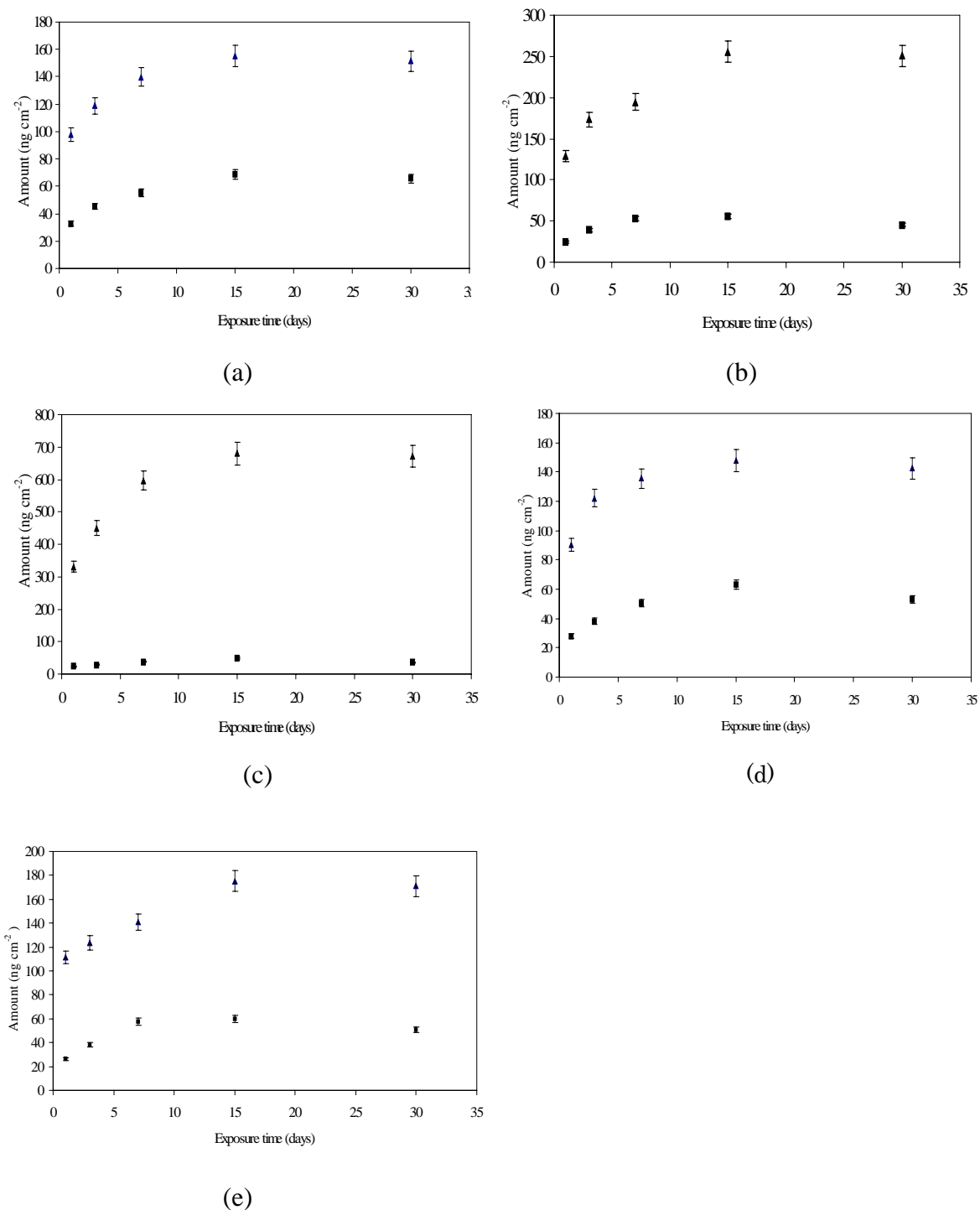
Fig. 4.3 The organic vapor absorption in polypropylene and poly(ethylene terephthalate) packaging material; a) acetone, b) 1-bromopropane, c) hexane, d) 2-propanol, e) trichloroethylene (▲ PP, ■ PET).

4.4   Effect of organic vapor on surface of packaging material

4.4.1 Effect of organic vapor on surface of polypropylene packaging material

Figs. 4.4 – 4.8 show SEM photographs of the surface of polypropylene packaging material exposed to organic vapor. The organic vapor attacked the surface of polypropylene packaging material when the absorption times were increased. An obvious damaged surface was found after 1 day of absorption time and got more sever after that, and then polypropylene surface was later cracked under organic vapor exposure. The presence of white tracks on polypropylene surface, possibly caused by etching solvents such as acetone was observed.
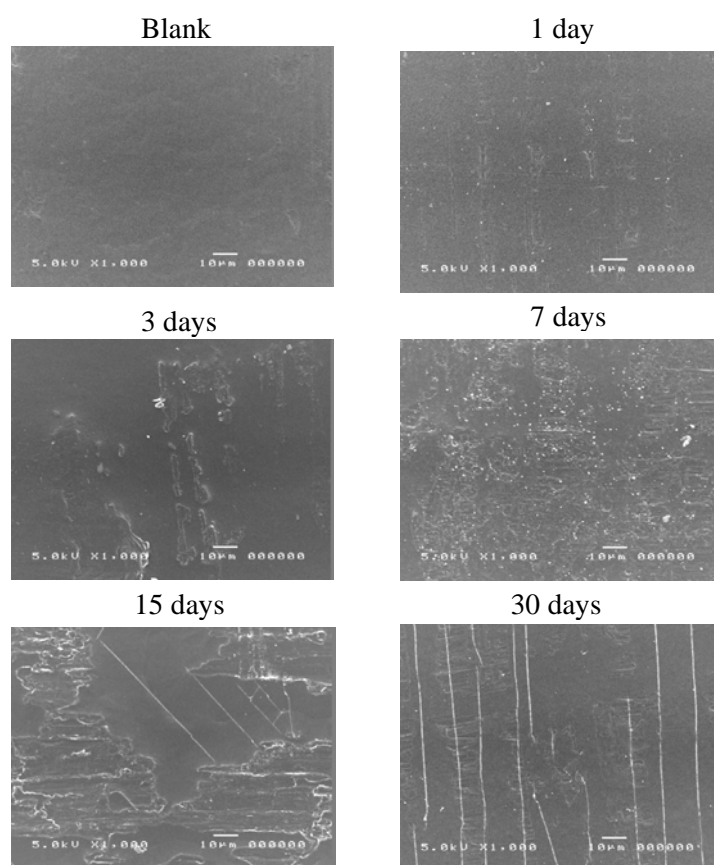

Fig. 4.4 SEM photographs showing the effect of acetone vapor on the surface of polypropylene packaging material
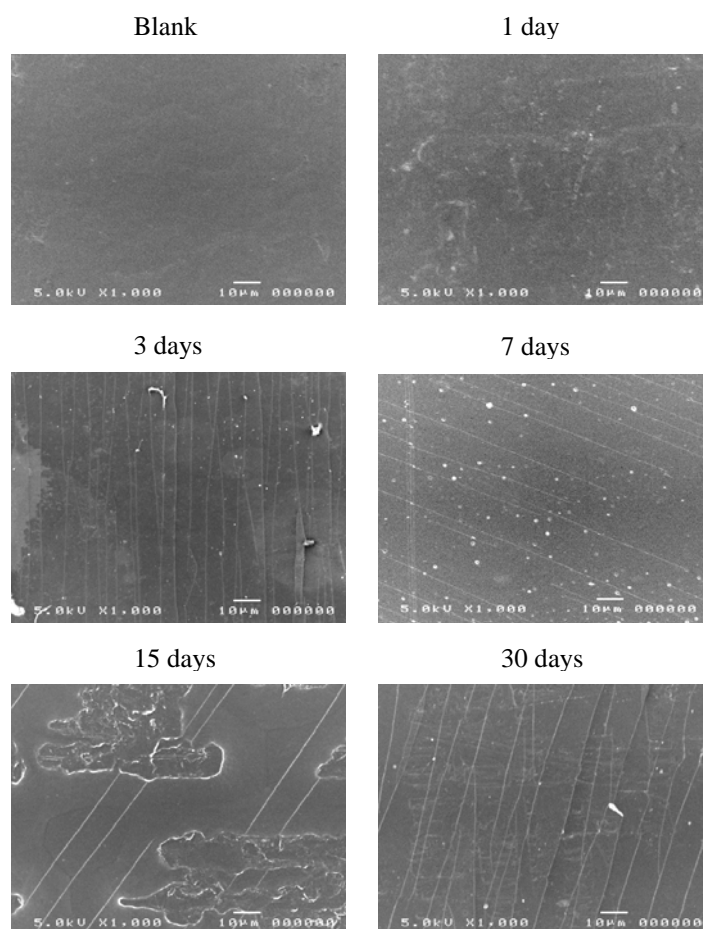
Blank | 1 day

3 days | 7 days

15 days | 30 days

Fig. 4.5 SEM photograph showing the effect of 1-bromopropane vapor on the surface

of polypropylene packaging material.

Blank

1 day

3 days

7 days

15 days

30 days

Fig. 4.6 SEM photographs showing the effect of hexane vapor on the surface of polypropylene packaging material.

Blank | 1 day

3 days | 7 days

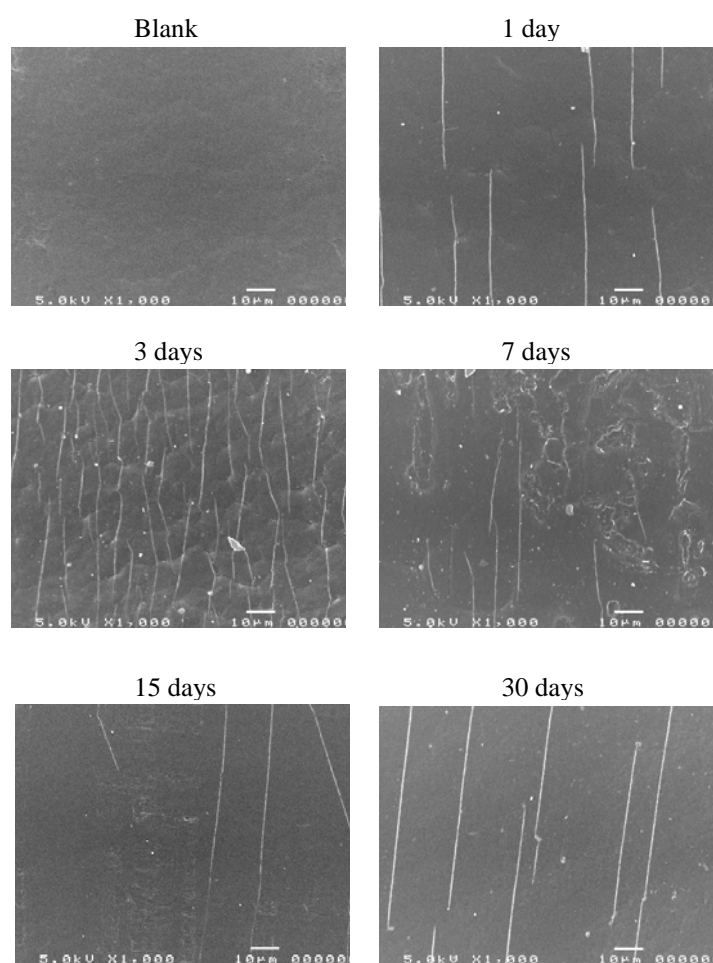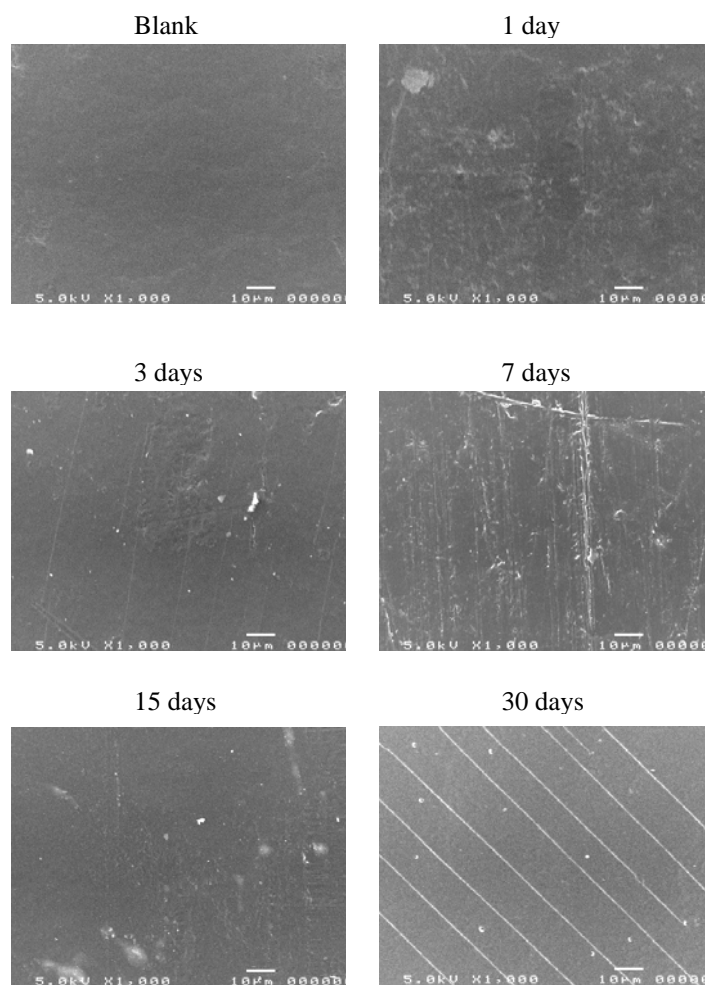15 days | 30 days

Fig. 4.7 SEM photographs showing the effect of 2-propanol vapor on the surface of polypropylene packaging material.
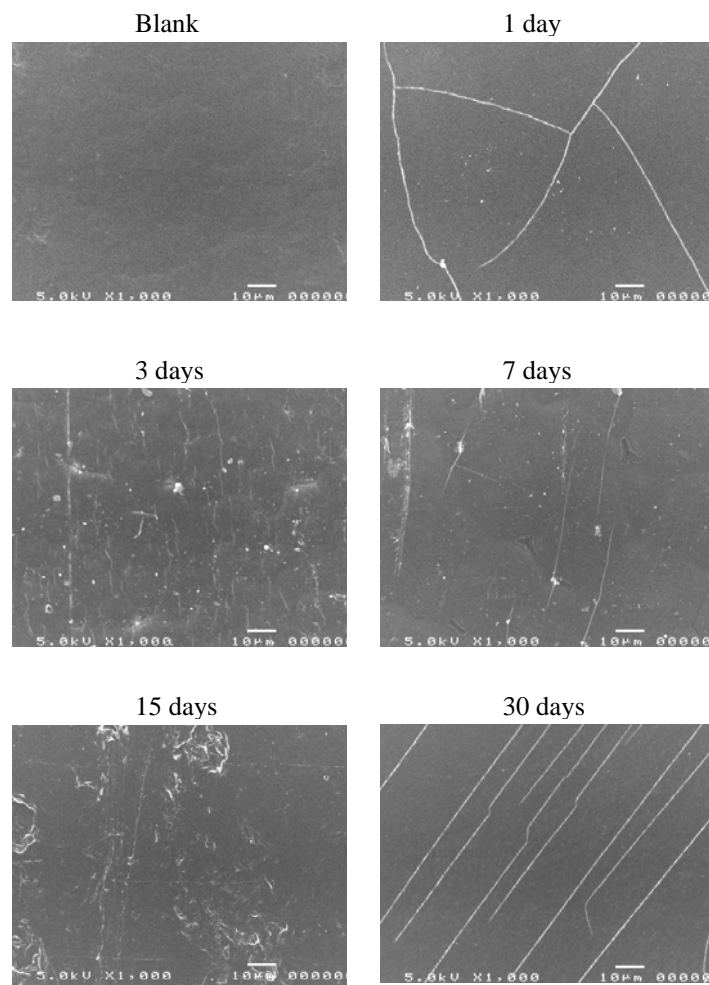
Fig. 4.8 SEM photographs showing the effect of trichloroethylene vapor on surface of polypropylene packaging material.

4.4.2 Effect of organic vapor on surface of poly(ethylene terephthalate) packaging material

Figs. 4.9 – 4.13 show the SEM photographs caused by the effect of organic vapor on the surface of poly(ethylene terephthalate) packaging material. The SEM photographs show that the surface of poly(ethylene terephthalate) packaging material was not damaged at all absorption times until 30 days of solvent exposure. The organic vapor cannot attack to the surface of poly(ethylene terephthalate) packaging material, suggesting strong surface properties of the PET.

Fig. 4.9 SEM photographs showing the effect of acetone vapor on the surface of poly(ethylene terephthalate) packaging material.

Blank

1 day

3 days

7 days

15 days

30 days

Fig. 4.10 SEM photograph shows the effect of 1-bromopropane vapor on the surface of poly(ethylene terephthalate) packaging material.

Blank

1 day

3 days

7 days

15 days

30 days

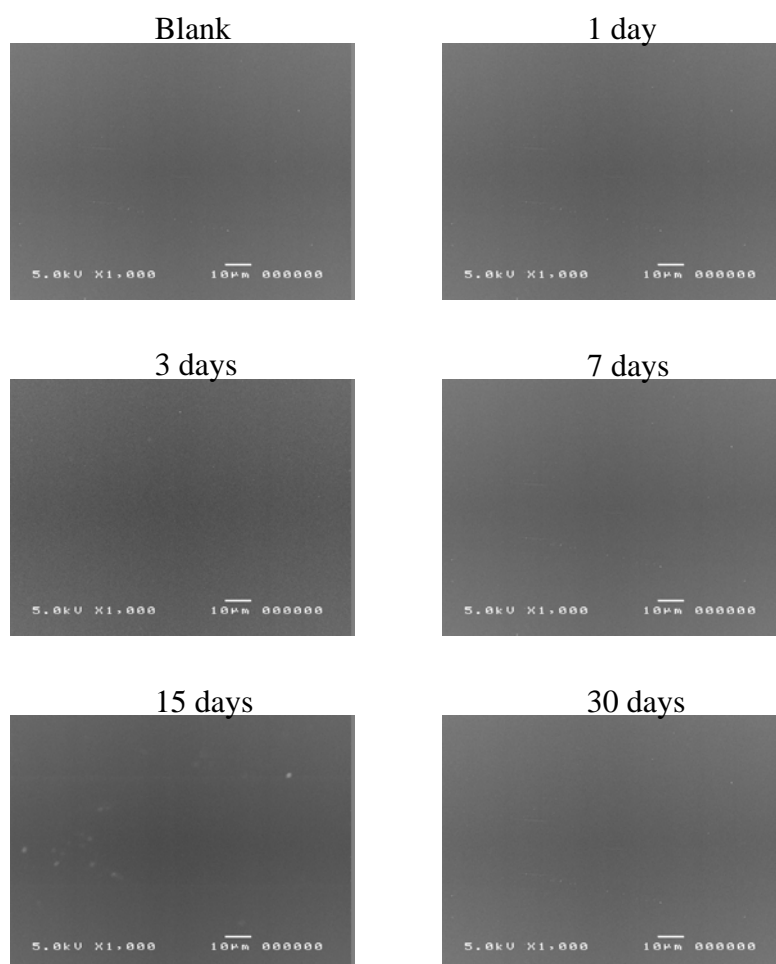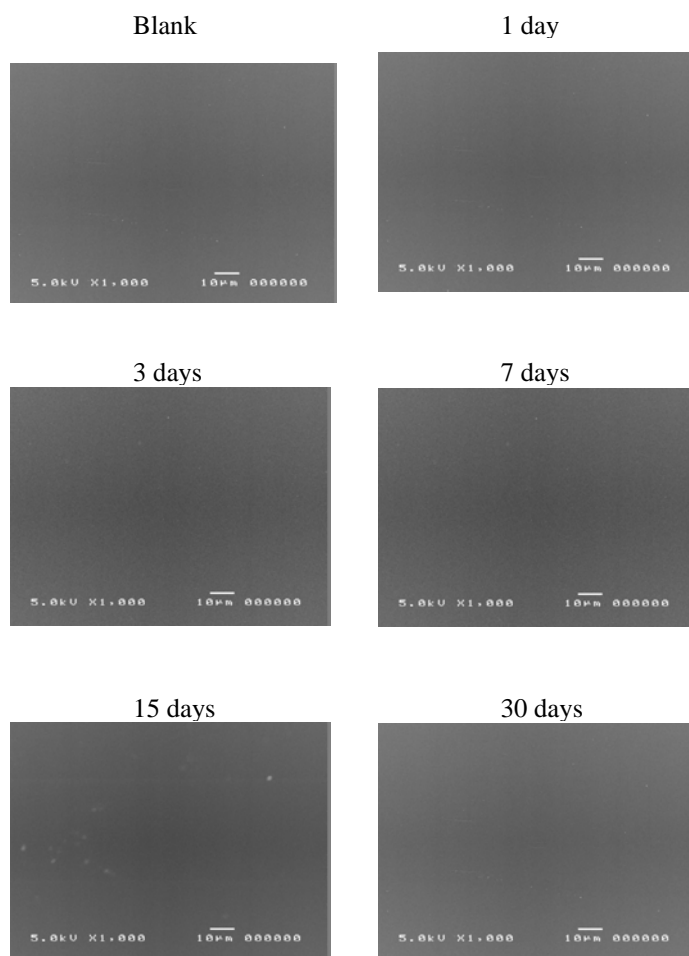**Fig. 4.11** SEM photographs showing the effect of hexane vapor on the surface of

poly(ethylene terephthalate) packaging material.

Blank

1 day

3 days

7 days

15 days

30 days

Fig. 4.12 SEM photographs showing the effect of 2-propanol vapor on the surface of

poly(ethylene terephthalate) packaging material.
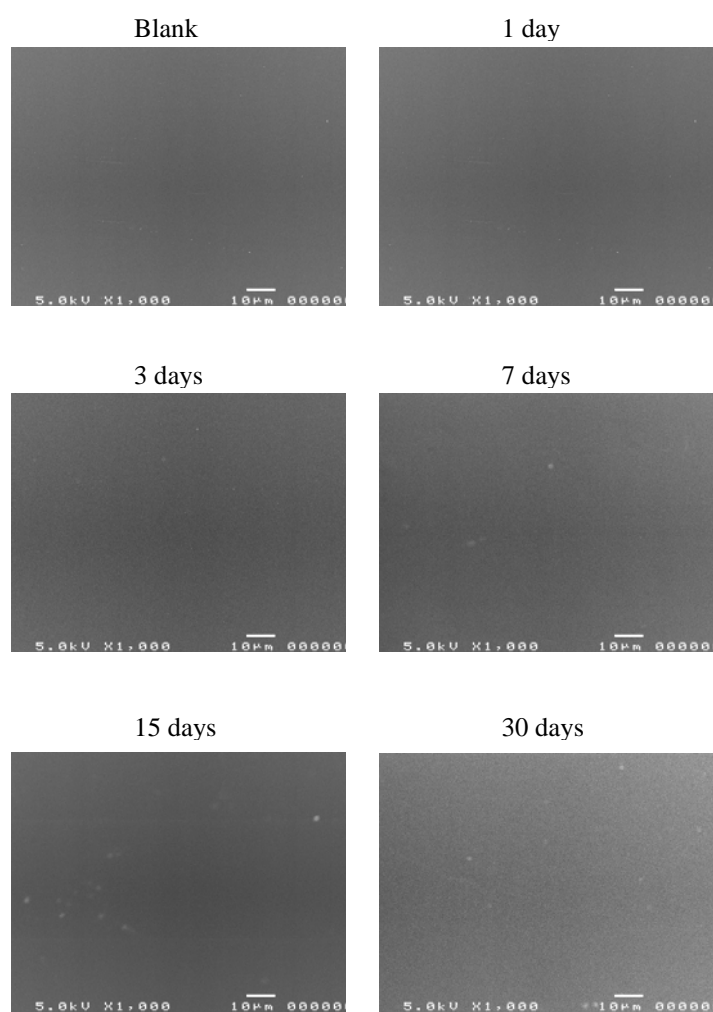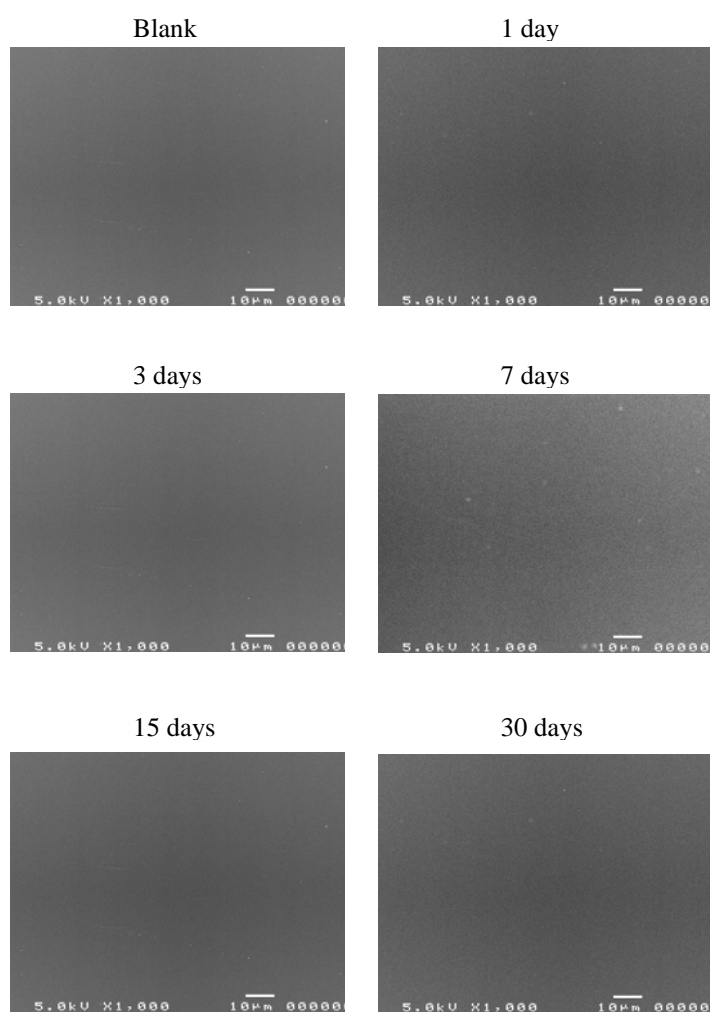
Blank
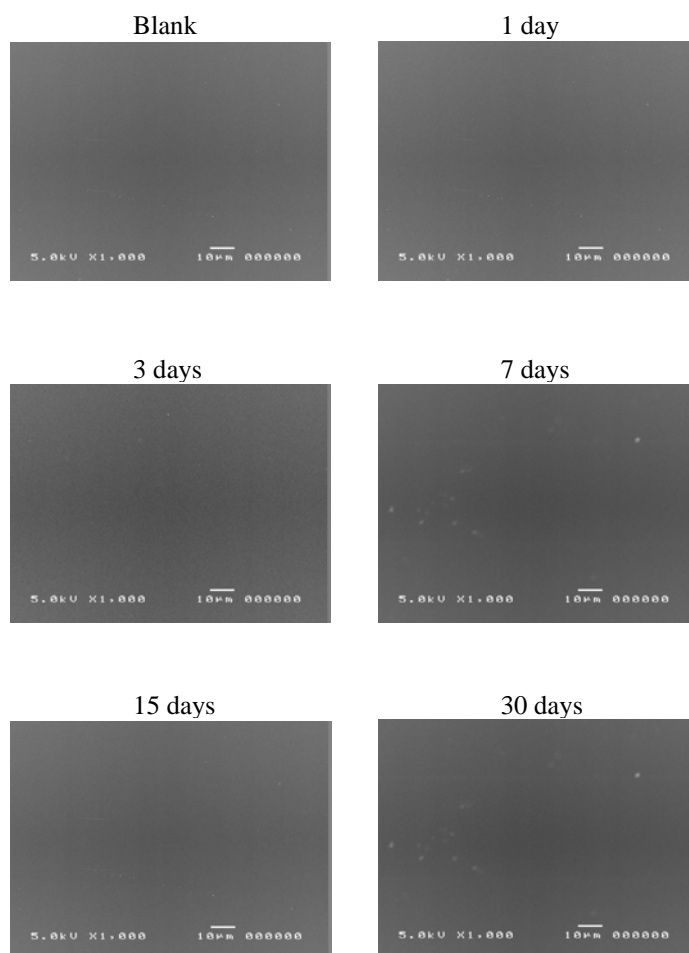
1 day

3 days

7 days

15 days

30 days

Fig. 4.13 SEM photographs showing the effect of trichloroethylene vapor on the surface of poly(ethylene terephthalate) packaging material.

Table 4.14 (a) presents the solubility parameters of organic solvents. Table 4.14 (b) presents the effect of organic vapor on surface of packaging material. The results showed that organic vapor affects the surface of polypropylene packaging. The polypropylene was cracked after 1 day by hexane vapor exposure. This is explained by that hexane has a solubility parameter closes to solubility parameter of polypropylene. These results correlates well with the high vapor pressure of hexane. However, the surface of poly(ethylene terephthalate) packaging was not damaged at all absorption times until 30 days of solvent exposure. The similar causes as those of section 4.3 are applied to this case.

Table 4.14 Relationship between solubility parameters of organic solvents

and plastic (PP and PET).

a) Solubility of material. [56]

Solvent	Solubility parameter (MPa)$^{1/2}$				$\left\lvert \delta_{solvent} - \delta_{plastic} \right\rvert$	
	δ_D	δ_P	δ_H	Total δ	PP	PET
Acetone	15.5	10.4	7.0	19.7	3.94	1.80
1-bromopropane	16.4	7.9	4.8	18.2	2.44	3.30
Hexane	14.9	0	0	14.9	0.86	6.60
2-propanol	15.8	6.1	16.4	23.5	7.74	2.00
Trichloroethylene	18	3.1	5.3	18.7	2.94	2.80
PP	15.76	0	0	15.76	-	-
PET	19.44	3.48	8.59	21.5	-	-

PP δ_T = 15.76 (MPa)$^{1/2}$

PET δ_T = 21.5 (MPa)$^{1/2}$

b) Effect of solvent – plastic interaction.

Solvent	Difference in Solubility parameter	Surface appearance	
		No changes	Cracked begun at
Acetone-PP	3.94		day 15th
Acetone-PET	1.80	X	
1-bromopropane-PP	2.44		day 3rd
1-bromopropane-PET	3.30	X	
Hexane-PP	0.86		day 1st
Hexane-PET	6.60	X	
2-propanol-PP	7.74		day 3rd
2-propanol-PET	2.00	X	
Trichloroethylene-PP	2.94		day 1st
Trichloroethylene-PET	2.80	X	

4.5   Effect of organic solvent vapor on chemical changes in packaging material properties

The effect of organic vapor absorption on chemical changes of packaging material was characterized by Fourier Transform Infrared Spectromety (FTIR).

4.5.1 Effect of organic vapor on polypropylene packaging material

Figs. 4.14 - 4.18 show the FTIR spectrum comparison of effect of organic solvent vapor on chemical changes of polypropylene packaging material. It is shown that the peak at 1080 cm^{-1} disappeared when the material was exposed to organic vapor from 1 day to 30 days. The results shown in the FTIR spectra indicate

that the chemical functionality of PP is changed except that for 2-propanol. The peak at 1080 cm^{-1} which is a C-C- stretch of CH$_2$ is disappeared, suggesting a change in the chemical structure.

Fig. 4.14 FTIR spectra showing effect of acetone vapor on chemical changes in polypropylene packaging material.

Fig. 4.15 FTIR spectra showing effect of 1-bromopropane vapor on chemical changes in polypropylene packaging material.
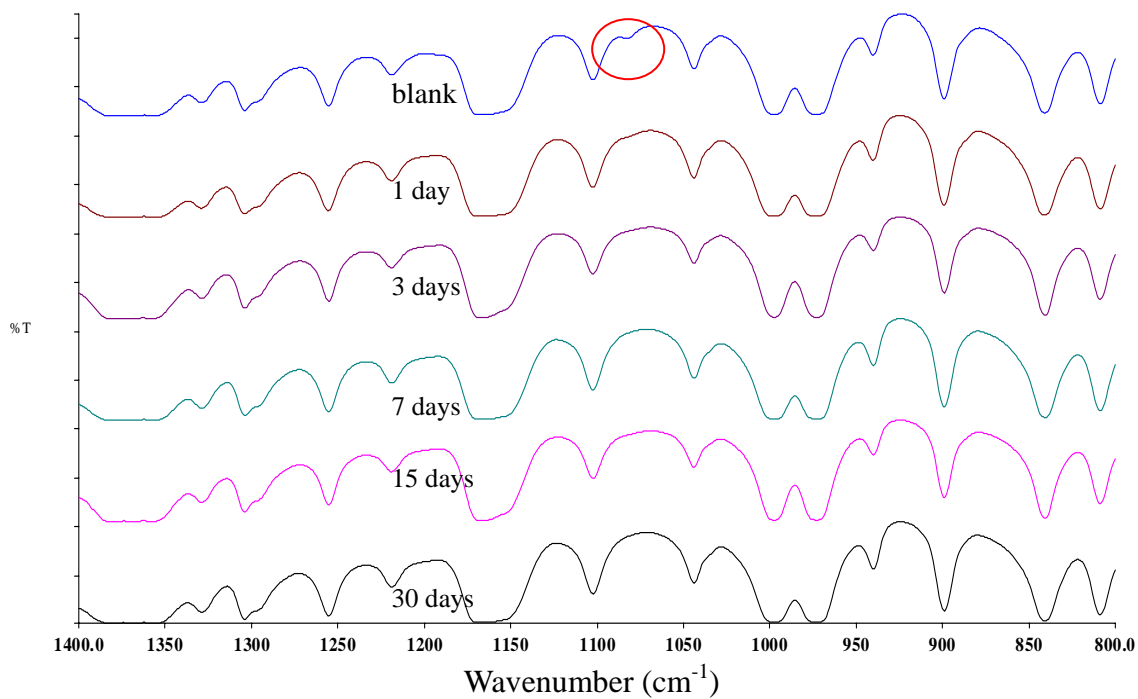

Fig. 4.16 FTIR spectra showing effect of hexane vapor on chemical changes in polypropylene packaging material.
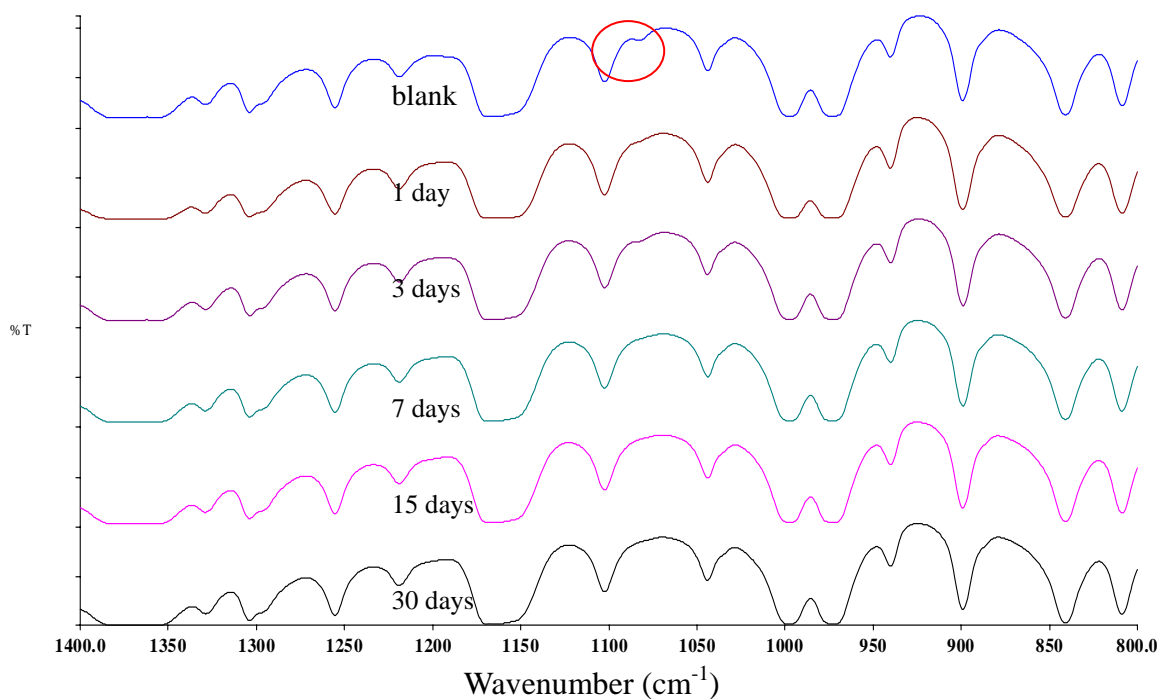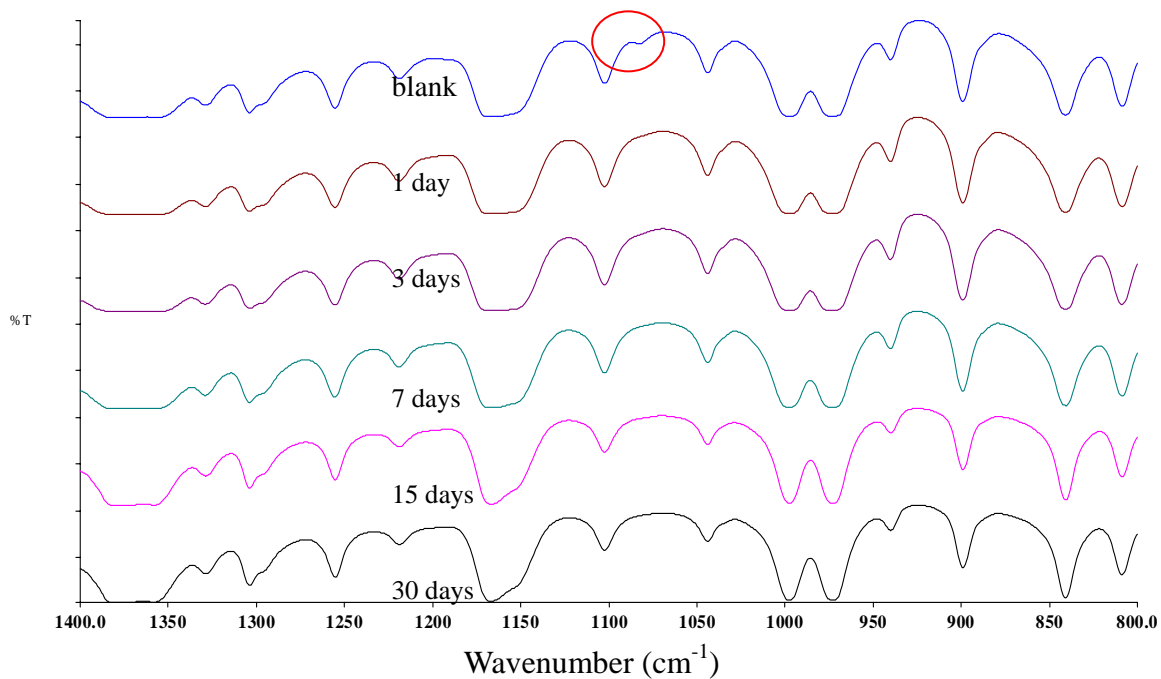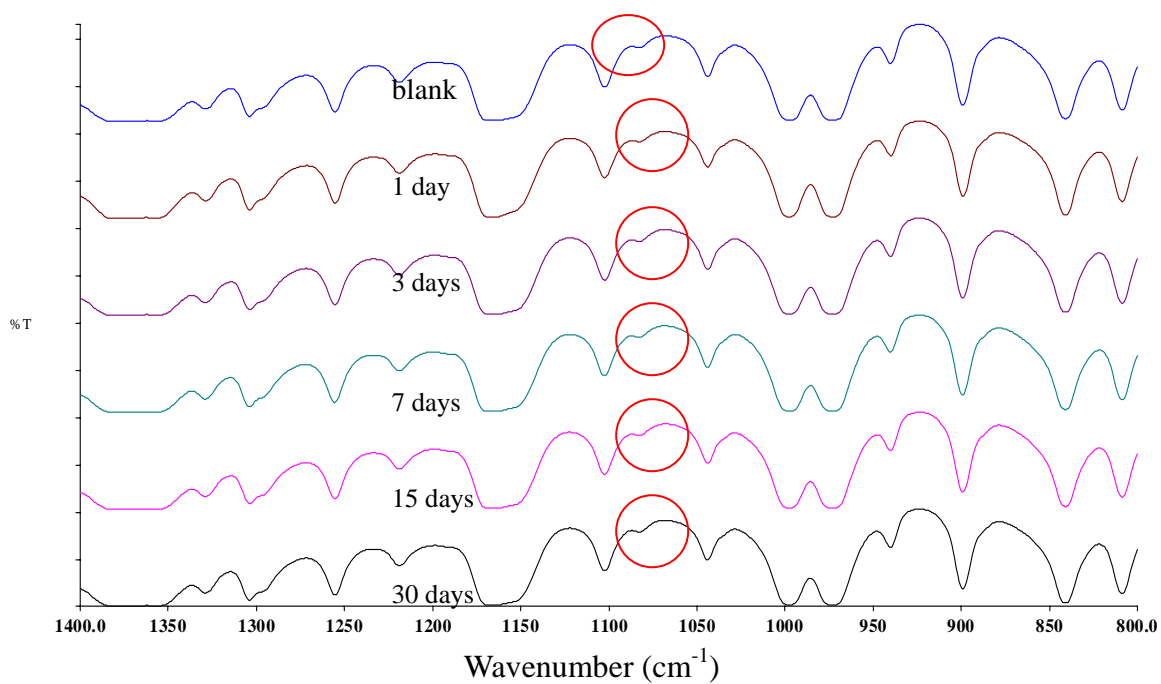
Fig. 4.17 FTIR spectra showing effect of 2-propanol vapor on chemical changes in polypropylene packaging material.

Fig. 4.18 FTIR spectra showing effect of trichloroethylene vapor on chemical changes in polypropylene packaging material.

4.5.2 Effect of organic vapor on poly(ethylene terephthalate)

Figs. 4.19 - 4.23 shows the FTIR spectra for the effect of organic vapor on poly(ethylene terephthalate) packaging material. All the spectra, were obtained by the exposed PET films with organic vapor for 1 to 30 days, are not changed at all. Because each FTIR spectrum can be superimposed with the others., i.e., organic vapor is inert to PET film. The organic solvent vapor cannot affect the PET due to its rigid structure. The similar causes as those of section 4.3 are applied to this case.

Wavenumber (cm^{-1})

Fig. 4.19 FTIR spectra showing effect of acetone vapor on chemical changes in poly(ethylene terephthalate) packaging material.

Fig. 4.20 FTIR spectra showing effect of 1-bromopropane vapor on chemical changes in poly(ethylene terephthalate) packaging material.

Fig. 4.21 FTIR spectra showing effect of hexane vapor on chemical changes in poly(ethylene terephthalate) packaging material.

Fig. 4.22 FTIR spectra showing effect of 2-propanol vapor on chemical changes in poly(ethylene terephthalate) packaging material.
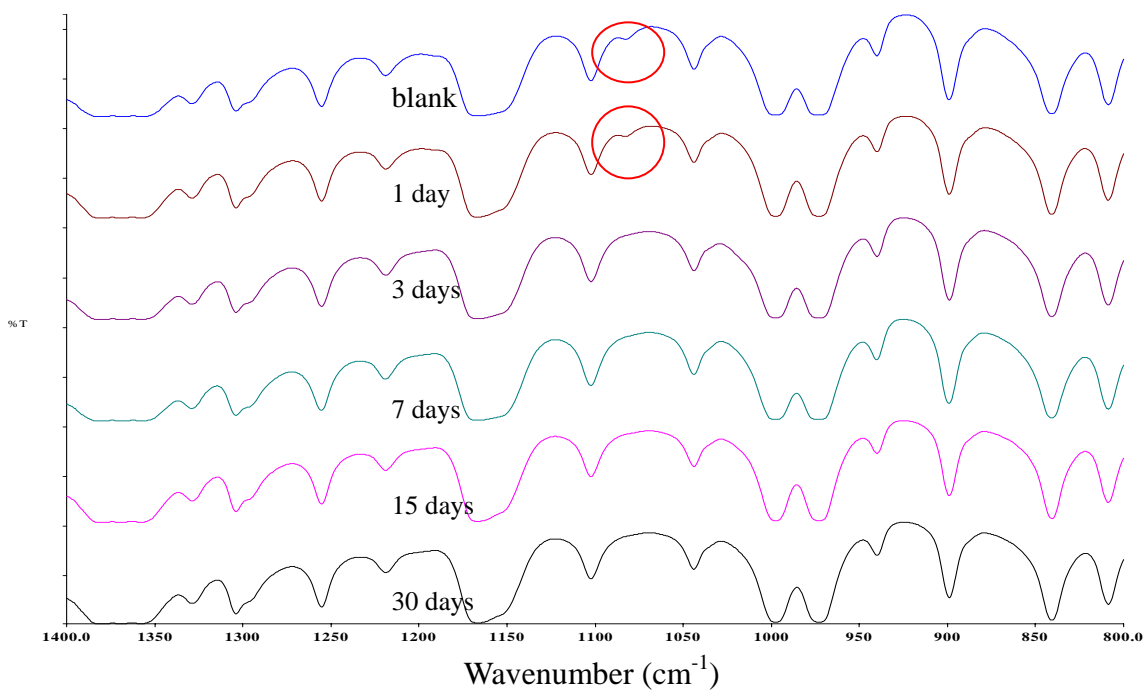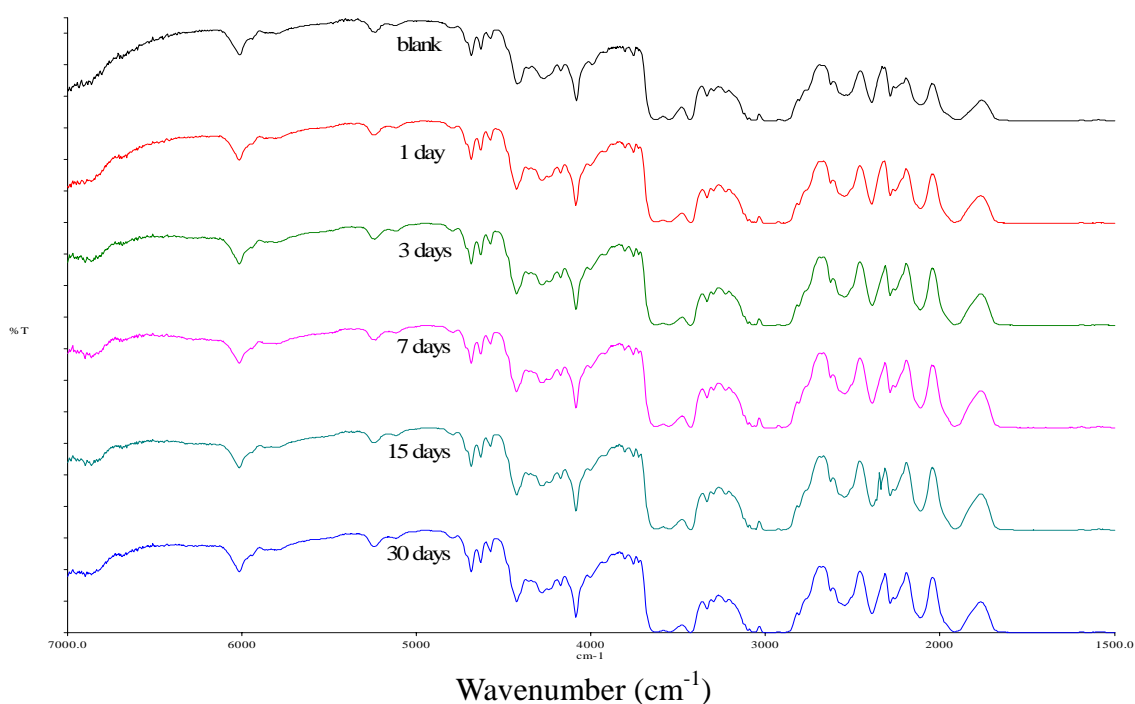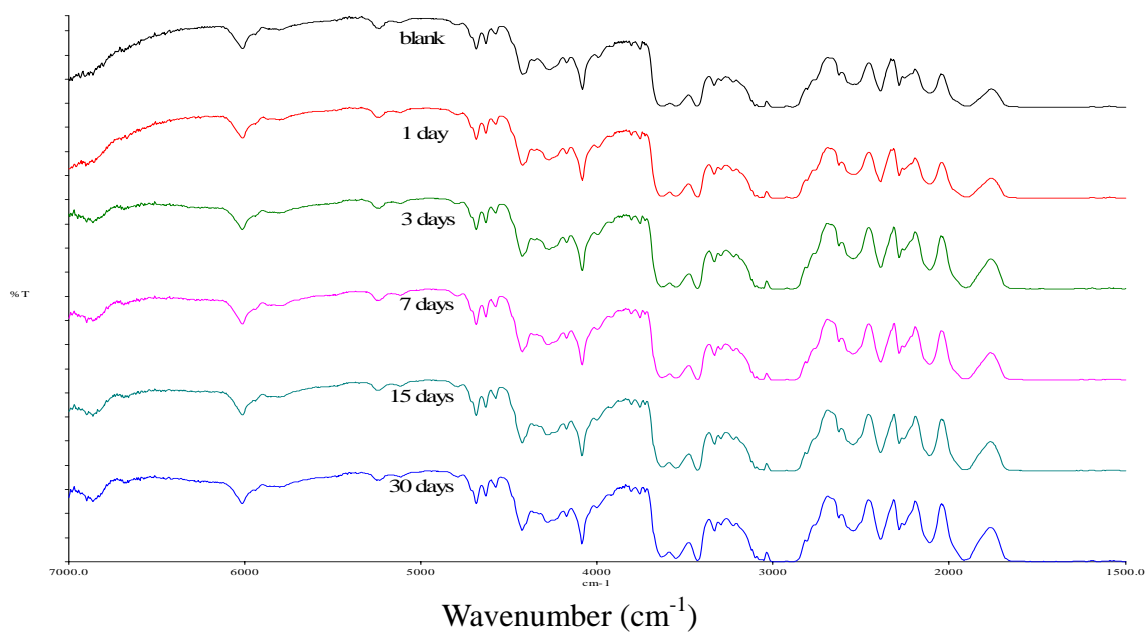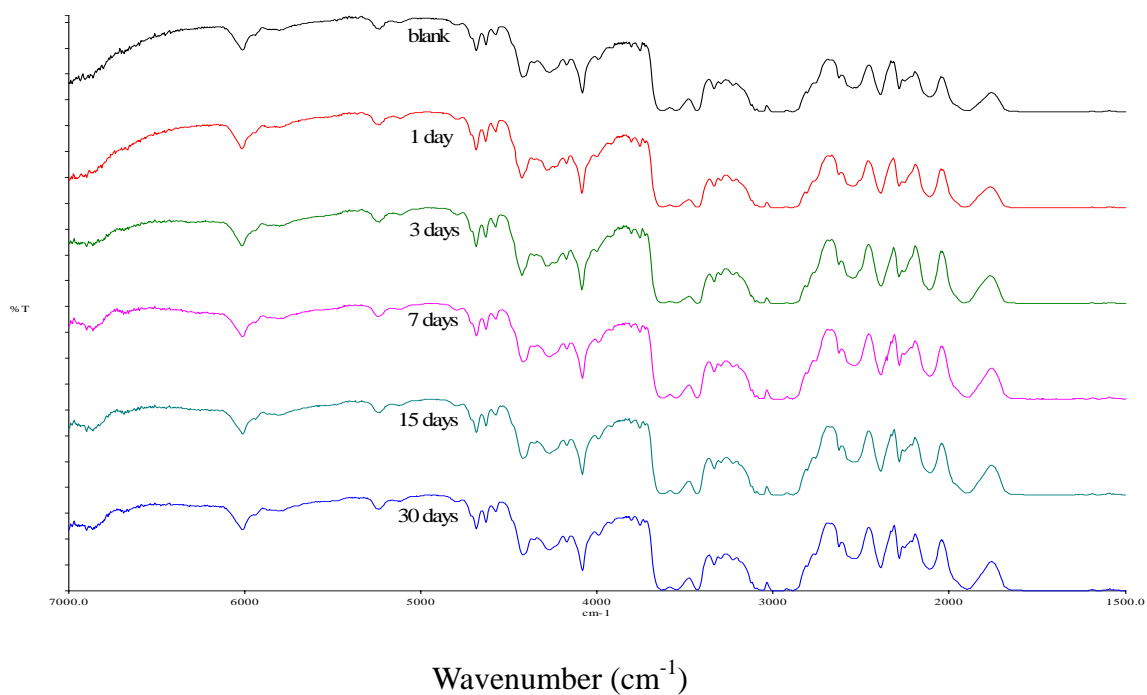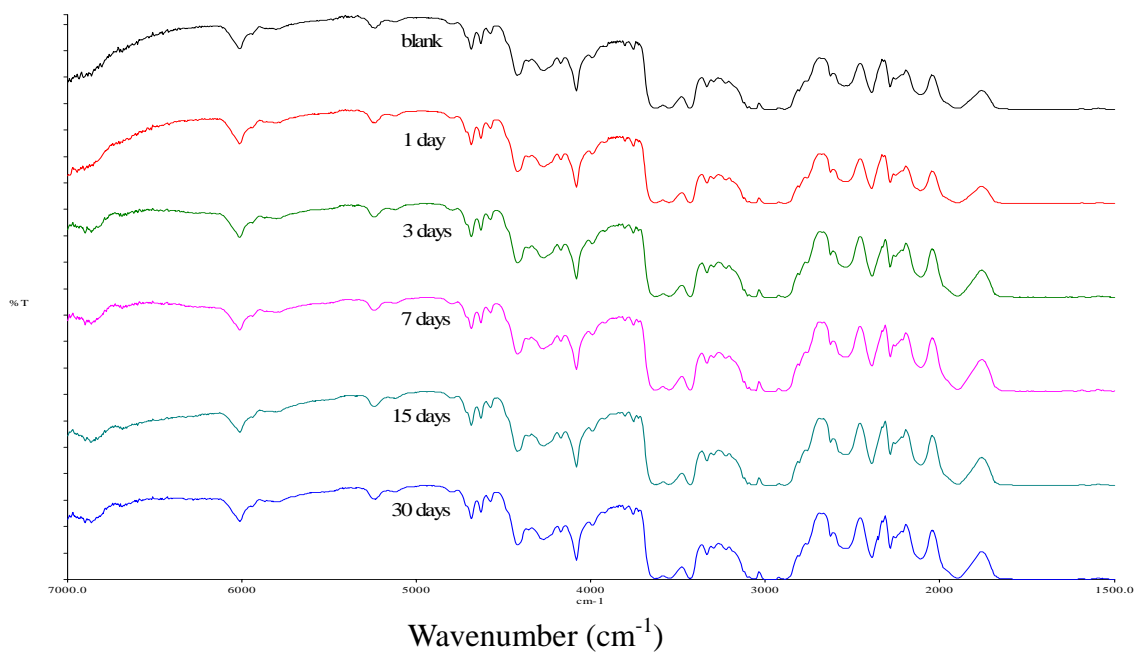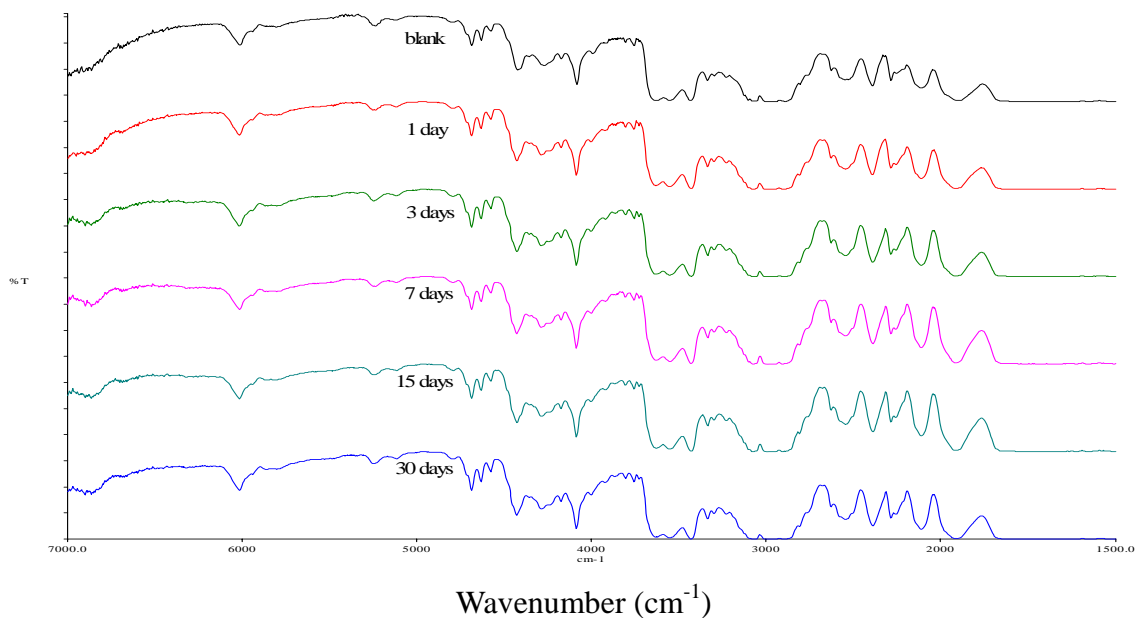

Fig. 4.23 FTIR spectra showing effect of trichloroethylene vapor on chemical changes in poly(ethylene terephthalate) packaging material.

4.6   Effect of organic vapor on thermal property of packaging material

The effect of organic solvent vapor absorption on thermal property of packaging material was characterized by Thermogravimetry and differential thermal analysis (TG/DTA).

4.6.1 Effect of organic solvent vapor on thermal property of polypropylene packaging material

Table 4.15 shows the effect of organic solvent vapor on thermal property of polypropylene. From the result, polypropylene packaging material as a blank material has a melting temperature at 167.7 ^{o}C and its exposed polypropylene has T_m decrease by about 2-3 ^{o}C under exposure with organic solvent vapor. These showed that the polypropylene packaging material was getting softer because of organic vapor absorption into the amorphous regions in the material.

Table 4.15 Effect of organic vapor on thermal property of polypropylene packaging material.

Absorption time (days)	Melting point (^{o}C)				
	acetone	1-bromopropane	hexane	2-propanol	trichloroethylene
1	164.6	165.1	164.7	164.5	164.2
3	164.2	164.8	164.5	164.4	164.7
7	165.0	164.9	165.1	164.9	164.9
15	165.0	164.9	164.5	164.6	165.0
30	164.9	164.9	164.4	164.6	165.0

The PP blank material (without exposure to organic solvent vapor) has a T_m of 167.7 ^{o}C.

4.6.2 Effect of organic vapor on thermal property of poly(ethylene terephthalate) packaging material

Table 4.16 shows the effect of organic solvent vapors on thermal property of poly(ethylene terephthalate). From the results, poly(ethylene terephthalate) packaging material used as a blank material has a melting point temperature at 247.7 ^{o}C. When the poly(ethylene terephthalate) packaging materials were kept under the vapor, thermal property of packaging material were not changed. The similar causes as those of section 4.3 are applied to this case.

Table 4.16 Effect of organic solvent vapors on the thermal property of poly(ethylene terephthalate) packaging material.

Absorption time (days)	Melting point (^{o}C)				
	acetone	1-bromopropane	hexane	2-propanol	trichloroethylene
1	247.0	247.3	247.6	247.0	247.0
3	246.6	247.1	246.8	247.4	246.8
7	247.0	246.9	247.2	246.9	247.3
15	246.7	246.8	246.9	246.8	246.9
30	246.7	246.9	246.9	246.9	246.8

The PET blank material (without exposure to organic solvent vapor) has a T_m of 247.7 ^{o}C.

4.7 **Effect of organic solvent vapor on dimension stability of packaging material**

The effects of organic solvent vapor absorption on dimension stability of the packaging material were characterized by measure in the thickness of packaging material.

4.7.1 Polypropylene packaging material

Table 4.17 shows the effect of organic solvent vapor to dimension stability of polypropylene packaging material. From the results, one piece of polypropylene packaging material used as a blank has thickness of 0.150 mm. After the exposure to organic solvent vapors, the thickness of polypropylene changed. Under the exposure, all specimens became thicker by 0.05 mm due to solvent swelling of PP films. Hexane and 1-bromopropane have solubility parameter close to that of the polypropylene; thus its vapor affects on the dimension stability of polymer is rather high. These results correlates well with the high vapor pressure of hexane.

Table 4.17 Effect of organic vapor on dimension stability of polypropylene packaging material.

Absorption time (days)	Thickness (mm)				
	acetone	1-bromopropane	hexane	2-propanol	trichloroethylene
1	0.175	0.175	0.175	0.150	0.175
3	0.175	0.175	0.175	0.175	0.175
7	0.175	0.200	0.200	0.175	0.175
15	0.200	0.200	0.200	0.200	0.200
30	0.200	0.200	0.200	0.200	0.200

4.7.2 Poly(ethylene terephthalate) packaging material

Table 4.18 shows the effect of organic solvent vapor on dimension stability of poly(ethylene terephthalate) packaging material. From the results, poly(ethylene terephthalate) packaging material used as a blank has thickness of 0.150 mm. Under the organic solvent vapor exposure for 1 to 15 days, the thickness is not affect in all vapors. The exposure time up to 30 days in the solvent vapor, the thickness increases by 0.025 mm except in hexane. Hexane vapor absorption by poly(ethylene terephthalate) did not affect the dimension stability significantly. Since hexane has the solubility parameter far from that of poly(ethylene terephthalate), leading to ineffective damage on PET surface. Finally, poly(ethylene terephthalate) offers mechanical strength, dimensional stability, moisture resistance, chemical resistance, clarity, stiffness, and barrier properties.

Table 4.18 Effect of organic vapor on dimension stability of poly(ethylene terephthalate) packaging material.

Absorption time (days)	Thickness (mm)				
	acetone	1-bromopropane	hexane	2-propanol	trichloroethylene
1	0.150	0.150	0.150	0.150	0.150
3	0.150	0.150	0.150	0.150	0.150
7	0.150	0.150	0.150	0.150	0.150
15	0.150	0.150	0.150	0.150	0.150
30	0.175	0.175	0.150	0.175	0.175

CHAPTER V

CONCLUSIONS AND SUGGESTION

In this research, the determination of Volatile Organic Compounds (VOCs) released from the plastic packaging material was investigated. Polypropylene and poly(ethylene terephthalate) packaging material were studied and investigated for improving cleanliness of electronic product. Hydrocarbons, esters and ketones were investigated with both packaging materials. The analyse were conducted using adsorption/thermal desorption gas chromatograph-mass spectrometry. The result showed that poly(ethylene terephthalate) contained less hydrocarbon and total VOCs than did polypropylene. The VOCs in the packaging materials are mostly produced by thermooxidative degradation of polyolefins and polyesters in the extrusion coating process. This process is necessary to achieve good adhesion properties, and entails depositing melting polymers on solid surfaces. The combination of high temperatures, often extreme shear stress and the presence of oxygen lead to the formation of organic radicals, and the combination of these radicals produces oxygenated compounds,

The effect of organic vapor absorption was also investigated with the packaging material (PP and PET). The organic vapors investigated are acetone, 1-bromopropane, n-hexane, 2-propanol and trichloroethylene. The relation between absorption time and organic vapor amount was identified. The analyse were conducted using adsorption/thermal desorption gas chromatograph-mass spectrometry. The result showed that poly(ethylene terephthalate) had less organic vapor absorption than did polypropylene. The organic vapor absorption in polypropylene can be ranked from the highest to the lowest as follows: n-hexane, 1-bromopropane,

trichloroethylene, acetone and 2-propanol. For the ranking of organic vapor absorption on polyethylene terephthalate are acetone, 2-propanol, trichloroethylene, 1-bromopropane and n-hexane. Solvent having a solubility parameter value close to solubility parameter of polymer gives the highest absorption. The effect of organic vapor absorption on VOCs released from packaging material was also investigated. The results showed that poly(ethylene terephthalate) has less hydrocarbon and total VOCs than does polypropylene.

In addition, the effects of organic vapor absorption to physical and chemical properties of packaging material were investigated. The organic solvent vapor did affect surface characteristic, chemical property, thermal property and dimensional stability of polypropylene packaging but they did not affect poly(ethylene terephthalate) at all. Since poly(ethylene terephthalate) offers mechanical strength, dimensional stability, moisture resistance, chemical resistance, clarity, stiffness, and barrier properties.

From this research, the appropriate packaging material for electronic product should be poly(ethylene terephthalate) which has a less amount of hydrocarbon and VOCs. In addition organic solvent vapor can affect insignificantly the physical and chemical properties of poly(ethylene terephthalate) packaging material.

For future work, VOCs analysis on Hard Disk Drive (HDD) products using poly(ethylene terephthalate) as a packaging material should be investigated and cleanliness of HDD products can be evaluated.

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