

UV curing of hybrid coatings

The sol-gel process

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TIIVISTELMÄ

Tämä opinnäytetyö tehtiin osana PlasmaNice-projektia. Projektin päämääränä on funktionaalisten nano-pinnoitteiden plasmadepostioteknikoiden kehittäminen useille kuitu- ja polymeeripohjaisille substraateille. Projektin tarkoitus on parantaa perinteisten fossiiliöljyn käyttöön perustuvien muovituotteiden kierrätettävyyttä ja/tai korvata ne uusilla bio-pohjaisilla sekä biohajoavilla materiaaleilla.

Opinnäytetyö koostuu kirjallisuuskatsauksesta, jossa perehdytään sooli-geeli tekniikan kemialliseen pinnoitamismenetelmään ja pinnoitteen UV-kovettamiseen; radikaalipolymeroitumiseen. Sooli -geelien ja hybridipinnoitteiden kemiallinen koostumus ja näiden yleiset kemialliset muodostumisreaktiot UV-kovettamistekniikan sovellusten näkökulmasta olivat kirjallisuuskatsauksen pääkohteena.

Hybridipinnoitteiden UV-kovettamisen reaktiokinetiikka oli käytännön tutkimuksen aiheena. Käytännön osuus koostui esimerkiksi spektroskoopisesta ja mikroskooppisesta pinnoitteiden karakterisoinnista.

Sekä kirjallisuusosuus, että käytännön työ tehtiin työsuhteen aikana. Opinnäytetyön kokeellinen osuus on luottamuksellinen, ja sitä ei julkaista viiteen vuoteen PlasmaNice-projektin ulkopuolisille jäsenille.

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ABSTRACT

This thesis was made as part of the PlasmaNice project which main objective is to develop equipment for in-line atmospheric plasma deposition of functional nanocoatings on various fibre- and polymer-based substrates. The project aims at the improvement of recyclability of conventional fossil fuel based plastics and/or the replacement by renewable bio-based (and biodegradable) materials.

Thesis consist on general literature overview about sol-gel chemical deposition method and UV curing; photoinitiated polymerization for hybrid coatings. Chemical composition of sol -gels and hybrid coatings and their common chemical reactions were researched from scientific literature from UV curable applications point of view.

UV curing reactions for hybrid coatings were studied in practice and experimental part consist of development work and for instance performing spectroscopical and microscopical characterization of hybrid coatings to support project aims.

Both literature and experimental work was conducted under employment relationship with VTT Technical Research Centre of Finland in Tampere. Experimental part of the thesis is confidential and therefore is not published for five years outside confidentiality agreement members or PlasmaNice project members.

Key words

Sol -gel, hybrid coating, UV curing

Preface

My acknowledgement goes to thesis supervisors from VTT; Juha Nikkola and Kalle Nättinen and Anne Ojala from TAMK. –Thank you for your patience and support.

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Abbreviations and symbols

BASF	German chemical company
cm ⁻¹	Wave number
ESCA	Electron spectroscopy for chemical analysis
FTIR	Fourier transform infrared spectroscopy
GC-MS	Gas chromatography -Mass spectrometer
HAP	Hazardous air pollutant
IPN	Interpenetrating polymer network
ITX	Isopropylthioxanthone
LED	Light emitting diode
M	Metal/metalloid
M ₀	Concentration at time=0
Nano	10 ⁻⁹
NMR	Nuclear magnetic resonance -spectroscopy
OH	Hydroxyl -group
ORMOSIL	Organically modified silicate
pbb	Parts per billion
PDMS	Polydimethylsiloxane
PE	Polyethylene
PET	Polyethylene terephthalate
PP	Polypropylene
R	Chemical (functional)group; rest
R _p	Rate of polymerization
Si	Silicon
TEOS	Tetraethoxysilane
UV	Ultraviolet (light)
UVC	Ultraviolet (light) wavelength 100-280 nm
VOC	Volatile organic compound
XPS	X-Ray photoelectron spectroscopy

Introduction

Growing interest in the use of variable sol-gel and UV curable coating techniques has raised need for facilitated introduction of new materials, improvements in manufacturing processes and developments of new analytical and testing methods. Unfortunately, information on these topics is scattered in journal articles, in conference and symposium proceedings, in workshop notes, and in government and company reports. This proliferation of the source material, coupled with the fact that some of the relevant publications are hard to find or are restricted, makes it difficult to identify and obtain the up-to-date knowledge needed to utilize UV curable coating techniques to their full advantage.

THEORY

1 Processing of sol-gel coatings

Most of the commercial applications utilizing the sol-gel processing takes place off-line batch processes. In industrial processes the finishing is made manually or with automated stage where parts of a final product are treated. The trend towards on-line processing with new products, methods and materials gives new opportunities and target areas for sol-gel applications. Especially, continuous sol-gel processing could be advanced in packaging applications where roll-to-roll processing is currently used. Figure 1 describes the typical coating application methods suitable for low-viscosity coatings, e.g. sol-gel coatings.

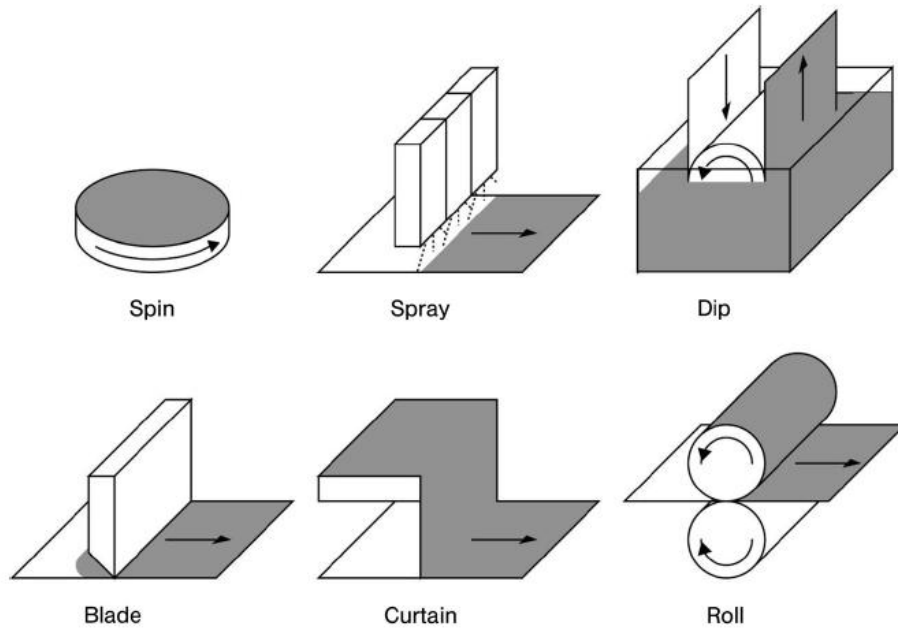


Figure 1. Coating application methods [Brabec, Dyakonov & Scherf]

The basics and advances in roll to roll processing lies in the possibility to combine different stages of manufacturing. It is cost effective to consolidate actions within production; instead of producing two different items with certain desired properties and combining them elsewhere, new impregnated materials could be developed and after development produced simultaneously on-line.

1.1 Sol-gels

The technology of sol-gel thin films has been around for over 40 years. The process is quite simple. A solution containing the desired oxide or non-oxide precursor is prepared. It is applied to a substrate by spinning, dipping, or draining, or spraying. The process is able to apply a coating to the inside and the outside of complex shapes simultaneously. The films are typically 200 nm -10 μm thick, uniform over large areas, and adherent. The sol-gel coating process is inexpensive, especially in comparison to any deposition techniques that involve vacuum. Coatings can be applied to metals, plastics, woods, papers and ceramics. Typically, the coatings are applied at room

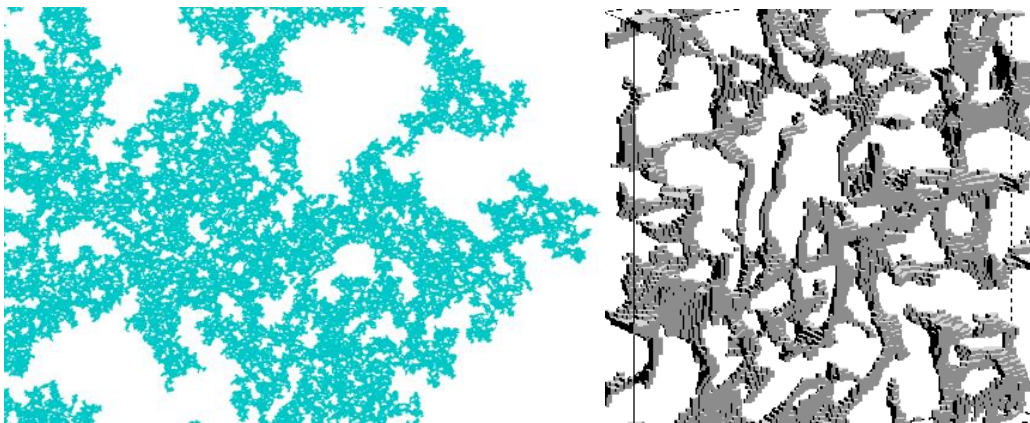
temperature, though most need to be calcined and densified by heating. Both amorphous and crystalline coatings can be obtained. [Vossen, Kern]

The basis for the sol-gel coating process is the hydrolysis of metal alkoxide compounds in alcoholic solutions. Alkoxide molecules exist as low molecular weight species, usually monomers or small oligomers, depending on the particular alkoxides used, the solvent and other factors. In principle, any precursors of a suitable compound which can be hydrolyzed could be used. The sol-gel reaction of these species occurs via hydrolysis of the M-OR moiety and polycondensation reactions involving the resulting M-OH group. Water acts as the “initiator” and is usually externally added. Water can also be generated in situ by condensation reactions such as the formation of esters by the condensation of carboxylic acids and alcohols. Acids or bases are used as catalysts for these reactions. The initial viscosity of the sol derived from polymeric precursors is rather low and in many cases is similar to that of water (- 1mPas). If the polycondensation reactions are allowed to occur to a significant extent, the original sol can transform into a gel. The reaction of metal alkoxides with water is known as the hydrolysis reaction. [Buschow et al.]

After the conversion into depositable colloidal sol by hydrolysis and polycondensation reaction, the sol can be applied on the substrates and cured during and after contact of the substrate with the coating solution. From a practical view, the reaction rate for the hydrolysis and condensation for the gel formation should be higher than the crystallization rate from the solution, in order to obtain uniform, transparent coatings. For this reason alkoxides are preferred.

[Klein 1988]

The formation of clusters of particles or monomers by random aggregation processes is a popular topic in modern physics. Fractal geometry is a concept which can give mathematic models to chaos –like forms in nature and it is based on self-replication; iteration.



Figures 1 and 2: Fractal dimension of the percolation
 [<http://blogs.nature.com/andrewsun/2008/09/17/percolation-fractal-and-physical-gelation>]
 and a model colloidal aerogel [<http://www.solgel.com/articles/jan01/aerogels.htm>]

Hybrid coatings

ORMOSILS (organically modified silicates) are organic-inorganic hybrid solids in which the organic component may be chemically bonded to a silica matrix. Somewhat similar to inorganic silicate glasses, the structure of the silica network can be modified by the presence of organic groups.[MacKenzie, BESCHER 1998]

In practically every published article in the field of sol-gel science and technology there is mention of potential applications for the materials under investigation.

This is also the case for Ormosils.

Sol-gel techniques have been widely used for the preparation of organic-inorganic hybrid materials. The inorganic network is obtained from metal-alkoxysilanes via hydrolysis and condensation reactions. The chemical reactions can be described schematically as follows:



The silanol group (Si–OH) produced by the hydrolysis reaction, (1), is converted into siloxane (Si–O–Si) crosslinks by either reaction (2) or reaction (3). Some silanol groups will remain after the chemical reactions have taken place because of incomplete condensation. [Han, Taylor & Mantle, M.D. and Knowles K. 2007]

Next figure shows the relation between physical properties and chemical composition as the most common system in this class of hybrids is that of PDMS (polydimethylsiloxane) and TEOS (Tetraethoxysilane). TEOS has been widely used as a precursor for silica in the sol–gel process to create the Si–O–Si bonds which are the backbone of silica-based organic–inorganic hybrid materials.

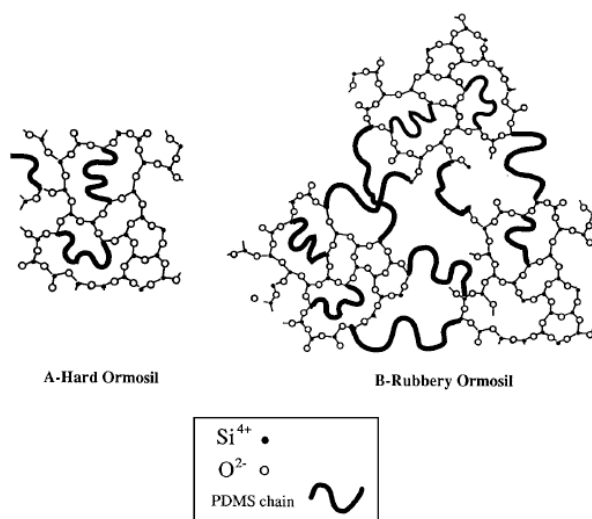


Figure 3. Proposed structures of SiO₂-PDMS hybrids for low (A) and high (B) PDMS content. [MacKenzie, BESCHER 1998]

Different mechanical properties become as an outgrowth from variation of the ratio of polydimethylsiloxane (PDMS) to tetraethoxysilane (TEOS) contents and processing conditions. With a low PDMS concentration, the ormosils are harder, stiffer and stronger than those with higher concentration of PDMS.

Commercial applications

Surface engineering will remain a growth industry well into the next decade because surface engineered products increase and improve performance, add functionality, reduce costs, improve materials usage efficiency, and provide performance not possible with bulk materials. Thin films thus offer enormous potential due to the following:

- Creation of entirely new and revolutionary products
- Solution of previously unsolved engineering problems
- Improved functionality of existing products; engineering, medical, and decorative
- Production of nanostructured coatings and nanocomposites
- Conservation of scarce materials
- Ecological considerations
- Reduction of effluent output and power consumption.

[Martin]

Nanoscale

There are various commercial applications for *nanoscale* sol-gel coatings. Coating types in nanoscale are usually for specialized products, not for on-line production. The range within these nanoscale sol-gel coatings, one of the more mature areas of nanotechnology, is wide starting from basic and applied research stage up to scaled up manufacturing and selling in the market.

Some examples:

- Anti-reflective, self-cleaning surfaces and barrier coatings
- Photocatalytic coatings
- Corrosion-protection systems
- Coatings for medical implants and non-fouling surfaces

[nanopost.com 2009]

1.2 Sol-gel application

The spraying method is based on the deposition of the sol from a sprayed aerosol, generated for example, by ultrasonic vibration. In order to achieve homogeneous films the solution and the processing parameters have to be adjusted carefully. The small droplets should not dry and gel before reaching the substrate. However, they should be able to coalesce on the substrate until a uniform layer is formed. Thus, the viscosity and the polymerization rate must not be too high; otherwise the coalescence process will stop and give rise to roughness or local thickness in homogeneities.

[Buschow et al.]

The thickness of sol-gel coatings is determined by the thickness of the parent liquid film when it abruptly increases its viscosity during the sol-to-gel transformation. It depends on the characteristics of the sol (chemical composition, concentration), on the deposition technique (dip-coating, spin-coating, spraying, etc.), and on the processing parameters (deposition speed, temperature, humidity, partial pressure of the solvent, etc.). [Buschow et al.]

1.3 Substrate surface pre-treatment

Adhesion and Bonding any type of compounds requires understanding of the mechanisms necessary for a good bond: surface energy and a chemical reactivity. Surface energy is the thermodynamic effect related to a material's intramolecular forces and is a determine factor on how an adhesive spreads across a surface. [Rhodes, Valencia & Bruner 2007] Surface tension energy is measured in dyne/cm =mN/m. Surface tension energy is the deciding factor on how well a liquid adheres to a polymer surface. For a proper bond to exist between a liquid and a substrate surface, the substrate's surface tension energy must exceed the liquid's surface tension energy by about 2-10 dyne/cm. [3DT LLC]

It is commonly accepted that the substrate's surface energy must exceed that of the adhesive for adequate contact. The better an adhesive spreads, the more intimate contact between molecules, thus allowing more reactive groups to bond.

1.3.1 Corona treatment as surface pre-treatment

Corona treatment is the modification of surface's surface energy and bonding ability through the excitation of molecules due to a corona or electrical discharge. When atmospheric air is exposed to different voltage potentials, electric discharge can develop; which can then trigger a collision of neutral molecules, causing the electrically loaded molecules to form a cloud of ionized air. The electrons generated in the corona discharge impact on the treatment with energies two to three times what is needed to break molecular bonds on certain plastics, or non-metallic surfaces. [Rhodes, Valencia & Bruner 2007]

1.3.2 Plasmas in continuous coatings processes

Plasmas can be used for surface activation and deposition. For example, glow discharge plasma used in deposition processes is a low-pressure gas which is partially ionized and contains approximately equal numbers of positive and negative particles. The character of such plasma is a consequence of the mass difference between the electrons and the ions. When an electric field is applied to an ionized gas, energy is transferred more rapidly to the electrons than to the ions. Furthermore, the transfer of kinetic energy from an electron to a heavy particle (atom, molecule, or ion) in an elastic collision is proportional to the mass ratio of electrons and heavy particles and therefore very small ($\sim 10^{-5}$). Consequently, at low pressures (low collision frequencies), the electrons can accumulate sufficient kinetic energy to have a high probability of producing excitation or ionization during collisions with heavy particles. The production of these excited species, and their interactions with surfaces and growing films, is one of the reasons that low pressure glow discharge plasmas are assuming an ever-increasing role in materials processing. Examples of application areas include the following.

- Sputter deposition
- Activated reactive evaporation
- Ion plating
- Plasma-assisted chemical vapor deposition

- Plasma-assisted etching
- Plasma polymerization

[Bunshah 1994]

Surfaces in contact with plasmas are bombarded by electrons, ions, and photons. The electron and ion bombardment is important and is used in materials processing, particularly during deposition and etching. Less is known about the influences of the plasma radiation. The relative number of ions and electrons which are incident on a surface depends on whether it is biased as a cathode, an anode, or is electrically isolated.

[Bunshah 1994]

2 Fundamentals of UV curing processes

As told earlier in most cases of using UV curing treatment, it is focused on an individual part of a final product as batch production. For example panels for furniture manufacturing are varnished with UV -curable resins. Since production speed and consistency, storage facilities and specialised products are currently more in to focus there is demand for on line coating in effective speed. It is known that curing with UV leads to high quality finishing and beneficial use of energy directly and indirectly.

Typically, the radiant energy produced by the UV lamp is focused by a reflector onto the coating. The UV energy striking the surface causes the photoinitiator to trigger the polymerization reaction. The material is usually solidified or dried when it exits the UV cure zone. The time, and consequently the space, required for cure is significantly less than thermal drying methods. Because the process relies on UV light to initiate the crosslinking of molecules, it does not evaporate any solvents nor significantly heat the substrate.

A UV curing process can provide finishers a number of advantages, including reduced floor space required, increased productivity and a high-quality finish. The UV curing market is growing rapidly because it is a "clean" technology that increases productivity compared to other traditional methods of curing. The UV curing process has a number of key attributes:

- **no solvents** -because cure is done by polymerization rather than by evaporation; VOC and HAP emissions are virtually eliminated
- **low temperature** -heat is not required
- **high speed** -cure is nearly instantaneous
- **energy efficient** -energy is invested only in the curing reaction, not in heating
- **easily controlled** -since inks and coatings do not "dry," they don't set up in printing/ coating equipment or change viscosity
- **quality finishes** -superior resistance to scratches and chemicals.

The use of UV curing presents a number of economic benefits over alternative methods. An economic benefit analysis for any one application may be substantially different from another. While they will vary with each application, cost savings may result from such factors as higher yield from 100% solids inks and coatings, reduced setup time, reduced waste and scrap, better use of space, reduction of work-in-process, increased productivity, energy savings, increased yield, reduction or elimination of VOC processing and improved product quality and performance. [Stowe 2001] Curing of polymer matrices by ultraviolet (UV) irradiation can be applied to a variety of processes in the production of composite components, as long as the component can be directly irradiated. The radiation can be generated by a variety of sources suitable for various specific applications and different curing strategies. The most frequently used radiation sources are mercury arc lamps. Because of the absorption of radiation passing through matter, the thickness of laminates for efficient application of UV curing is limited. Wet lay-up techniques, vacuum infusion type processes with UV-transparent membranes, filament winding, and prepreg processes have been adapted to UV curing. Unlike in thermal curing, the curing time is in the order of magnitude of minutes rather than hours, which means a significant reduction in cycle time [Amerio et al. 2009]

The market for ultraviolet curing technology has been growing at double-digit rates in the last 10 years. The main reason for such a rapid technological growth of UV curing is its unique process characteristic, which allow UV-coating to be applied on virtually any substrates, including plastic, metal, composite, wood, paper, leather, vinyl, glass, magnetic recording tape and even human teeth. The original driving forces behind the commercialisation of UV-technology were energy saving and freedom from solvents.

These benefits are complemented by high productivity and subsequently higher profits that can be achieved with the increased line speed, just-in-time benefits and immediate “pack and ship” capabilities. [Shukla et al. 2004]

It has been reported that radiation curing systems have performance advantages of scratch, abrasion, solvent, and chemical resistance over thermally cured coatings. Some UV-curable systems have been reported to have higher gloss than its thermally cured counter parts. Moreover, the UV-curable system has the advantage of a rapid cure.

UV curing equipment can be made with LED (light emitting diode) –technology. UV LED Curing Advantages are lower operating costs with no bulbs or other consumables, energy-efficient with low electricity consumption and no air extraction, safer operation with very low heat generation and no UVC wavelengths, instantaneous and constant output with no warm-up time, environmentally friendly with no ozone emissions or dangerous mercury, compact and scalable design for ease of integration, and much longer service life with LED chips lasting 10,000 plus operating hours.

2.1 UV curing in the food packaging industry

UV-curing is used extensively on the exterior of paper and paperboard food packaging, when package construction offers an effective functional barrier between the cured surface and the food contents. UV curing has not reached its full commercial potential in plastic and film food packaging applications. It is due to missing approval for usage of these materials creating the food package applications. Monomers, oligomers and initiators typically used are not necessarily suitable for food packing applications. The unfamiliarity of the end users with these materials also has an affect for the demand. Migration of the photoinitiator through material layers to food is a major concern. Finding and creating photoinitiators that does not posses any toxicity might be the solution instead of trying to bind or vapour out the initiator chemicals that are not proven suitable for food packaging.

For example in 2005 there was an incident with photoinitiator isopropylthioxanthone (ITX). ITX is used in the curing process during ultraviolet printing processes. Nestlé

has been using the same container from Tetra Pak for the milk for the past 10 years and it was the first time the problem had been noticed.

The problem occurred during what he called a "routine" test for other substances by an Italian laboratory. The laboratory found the traces of ITX in the milk products and regulators told Nestlé about the problem. In November 2004 patent application in the US, Sun Chemical noted: "In recent years, thioxanthone derivatives, particularly isopropylthioxanthone (ITX) and diethylthioxanthone, have been extensively used in UV curable printing ink applications. However, these are not entirely satisfactory because, following curing, unreacted thioxanthone derivatives of this type have a tendency to migrate from printing inks into, for example, packaged foodstuffs." EU legislation¹ due to come into force setting migration limits of substances for multi-layer food packaging led it to conduct the studies. The new directive sets migration limits of 10 pbp for non-evaluated substances and 50 pbp for substances for which tests had been conducted and were shown to be safe. [Ahmed 2005]

¹(Commission Regulation [EC]. 2006. No 2023/2006 of 22 December 2006 "on good manufacturing practice for materials and articles intended to come into contact with food." Off J Eur Union L384/75.)

2.1.1 UV initiators suitable around food –the search continues

The question about food contact suitable and totally secure photoinitiators is still open. The focus is more on to new low migration photoinitiators: Type I initiators e.g. α -hydroxyketones and type II initiators e.g. benzophenones can be adjusted to be a low migrating initiators by adding their molecular weigh. Also Sulfonium salts for cationic UV curing with high molecular weigh won't release harmful compounds like benzene or toluene.

Various studies about migration of photoinitiators from packaging to food exist. Lesser to that is found articles about efficient initiators that are suitable for food packaging not just concerning initiators migration characteristics, as well initiator as a safe chemical compound. Low migration properties can be achieved by photoinitiator selection (high reactivity, new high molecular weigh photoinitiators), by optimization of the formulation (avoid excess of photoinitiators, formulation to be fine-tuned including oligomers and monomers) and by proper working conditions during production (ensure

high cure efficiency: UV bulb & reflector control, process control - light dose intensity and printing speed, favouring working under oxygen reduced atmosphere).

Migration usually describes a diffusion process, which may be strongly influenced by an interaction of components of the food with the packaging material. Food components, particularly fat, that migrate into plastics, like PE or PP, will considerably increase the mobility of plastic components, thus, enhancing the migration into the contained food. Migration is a health issue and is a legal problem in most countries. In an attempt to harmonize legislation, the EU (European Union) and the FDA (Food and Drugs Administration) initiated global control through positive lists of substances that can be used, while restricting substances with toxic potential. The general purpose of the legislation is to ensure consumer safety.[Arvanitoyannis, Bosnea 2004]

Generally, the migration is considered to be a process where polymerization residues or stabilizers can diffuse through the polymer matrix to the surface. Diffusion is considered to be one of the main mechanisms for the transfer and migration of chemical compounds from packaging materials to food. The migration of ingredients from packaging material into food is undesirable. However, a certain transfer is unavoidable, because most foodstuffs are packed prior to their purchase by the consumer. The contamination is usually due to the dissolution in the food that comes in contact with the migrated stabilizers on the polymer surface. The term “migration” is used to describe the process of mass transfer from a food packaging material to its contents. During this process, a packaging material comes in contact with food, and though its mechanical or diffusion properties are not altered, it may adversely affect the organoleptic properties of the packaged food.

[Arvanitoyannis, Bosnea 2004]

2.2 Migration studies

Study by Pastorelli et al. investigates the migration of benzophenone. Benzophenone is one of the two component composing the commercial application described earlier; IrgaCure500[®]. Benzophenone is also one of the most commonly used photoinitiators, which are mostly used in UV-cured inks for which drying times are much shorter than

for conventional solvent or water-based coatings. In study the benzophenone levels were determined in different packaging materials used for cakes, to evaluate the safety of printed paperboard intended for food contact. Plastic sleeves commercially used for this specific food application are normally made of PP. In the study barrier properties of a commercial available PP of 38 μm and two multilayer Films: PET-SiO_x/PE and PP/EVOH/PP were compared. The properties were tested under two different time and temperature conditions (70°C for 2 days and 40°C for 10 days). The multilayer containing PET-SiO_x/PE turned out to be perfect barrier for no migration was detected on target cake after 2 or 10 days. For other multilayer PP/EVOH/PP there were 45 $\mu\text{g/g}$ after 10 days in 40°C and 1 800 $\mu\text{g/g}$ after 2 days in 70°C. Migration level for conventional PP was high: 1 400 $\mu\text{g/g}$ at 40°C and 3 800 $\mu\text{g/g}$ at 70°C. [Pastorelli et al. 2008]

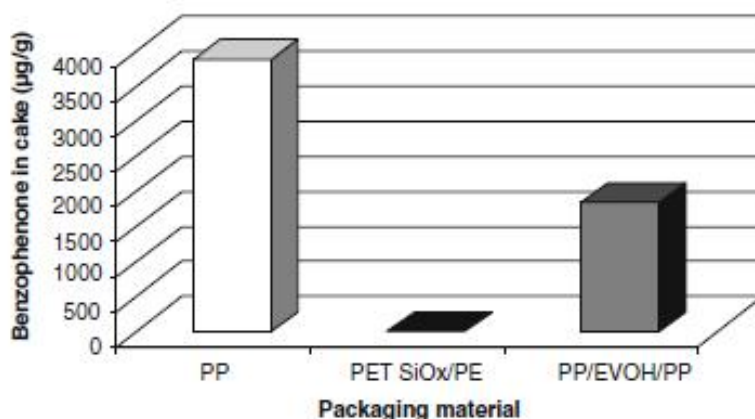


Figure 5 : Diffusion of benzophenone into cakes, at 70 °C for 48 h [Pastorelli et al. 2008]

Although the boiling point of benzophenone is high (305.4 °C) and its vapour pressure (0.56 Pa at 40 °C) very low, benzophenone migrates easily in the vapour phase from the additivated source to the cake through the PP film. Suitable multilayer packaging materials could represent a good way of guaranteeing better functional barrier properties for more effective reduction of potential diffusion of benzophenone (or molecules that behave similarly) from printed paperboard boxes to foodstuffs, especially relatively dry foodstuffs that may be particularly sensitive to such diffusion. [Pastorelli et al. 2008]

Other case study for Benzophenone as a curing of inks with ultra-violet (UV) light points out the migration of photoinitiators. UV-cure inks contain typically 5–10 per cent photoinitiator. Only a small portion of the initiator is used up during the curing process. Benzophenone can therefore remain in the printed material. The use of UV-cure inks for printing cartonboard has become widespread because the fast cure permits online cutting and folding, enabling rapid production of finished packaging. In a UK survey reported in 2000, 350 samples of food packaged in printed cartonboard were purchased from retail outlets. The packaging was analysed for residues of benzophenone, using solvent extraction and GC-MS analysis. One hundred and forty three packaging samples contained measurable benzophenone. Seven of the 143 samples were in the concentration range 0.05 to 0.2 mg/100 cm², 60 of the 143 were in the range from 0.2 to 0.8 mg/100 cm² and the remaining 76 packaging samples contained benzophenone in the range from 0.8 to 3.3 mg/100 cm². Seventy-one samples were then selected at random from the 143 packaging samples that contained benzophenone, and the food contained in these 71 packages was analysed for benzophenone. Benzophenone was detected in 51 of the 71 food samples. Twenty-nine samples contained benzophenone at 0.05 to 0.5 mg/kg, 17 samples were in the range of 0.5 to 5 mg/kg and three exceeded 5 mg/kg. The highest level was 7.3 mg/kg. Two samples contained levels that were detectable but not quantifiable.

When there was no benzophenone in the packaging there was none detected in the food. However, there was not a clear numerical correlation between levels of benzophenone in cartonboard and food. Differences in the composition of the foods tested may have been important in this respect, along with other factors such as the storage time, the storage temperature, the extent of any direct contact made between the food and the package, and the presence or absence of any barrier material between the printed cartonboard and the food. The results confirmed that benzophenone can migrate from printed cartonboard to food. Research has shown that benzophenone can be present in printed cartonboard packages at up to 0.7 mg/100 cm² and can migrate to foods packaged in this material even during frozen storage, up to 0.4 mg/kg. For frozen foods in microwavable packaging, the extent of migration into the food during storage and subsequent heating was shown to increase further, with levels of benzophenone after heating ranging up to 1.0 mg/kg.

At the end the study emphasises that the potential for migration to dry and frozen foods cannot be ignored. It also illustrates that barrier layers may be ineffective in preventing migration. Although the inks were applied to the outside of the cartonboard, the board itself presented little if any barrier to migration and even some thin plastic films were inadequate barriers if made from high permeability plastics like polyethylene. [Watson 2001]

3 Photoinitiation with UV light

The term photopolymerization means the initiation by light of a chain polymerization process. In the more general sense, photopolymerization implies the increase of molecular weight caused by light and includes the photocrosslinking of pre-existing macromolecules. Vinyl polymerization can be initiated by ionic species as well as by free radicals, but almost all examples of photopolymerization are of a free-radical character. Photochemical production of primary radicals needs low temperature (10–40 °C), unlike thermal free-radical initiators which generally occur above 40 °C.

Consequently, photopolymerization can be carried out at very low temperatures. Hence chain transfer processes leading to branched macromolecules will be absent.

Photopolymerization at low temperature yields the low-energy stereospecific polymeric species.

Photopolymerization, the utilization of electromagnetic radiation (or light) as the energy source for polymerization of functional *monomers*, *oligomers*, and *polymers*, is the basis of important commercial processes with broad applicability, including photoimaging and ultraviolet (UV) curing of coatings and inks. These processes require light that is absorbed by the system and utilized to effect the formation of new chemical bonds:

Photoinitiators, photocrosslinking agents, and photocrosslinkable polymers.

Photoinitiators absorb light in the UV–visible spectral range (250–450 nm) and convert this light energy into chemical energy in the form of reactive intermediates, such as free radicals and reactive cations, which subsequently initiate polymerization of functional monomers to form linear polymers, whereas the multifunctional monomers give three-dimensional crosslinked networks.

[Manmeet, Srivastava 2002]

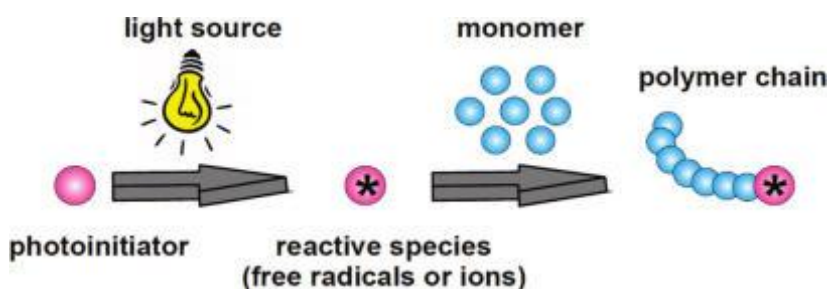


Figure 6: General Presentation of Photoinitiated Polymerization [Yusuf, Steffen, Jockusch and Nicholas J. Turro 2010]

3.1 Curing rate in UV curing processes

The rate of the curing process depends on the following:

Monomer compounds in the UV resin - Each monomer cures at a different rate, depending on the amounts and compositions of sensitizer, pigment, and chemical additives. **Coating Thickness** - The thickness of UV coating is not directly proportional to exposure time. The amount of UV energy inside a layer of coating decreases exponentially with depth. A two-fold increase in the thickness requires a ten-fold increase in UV intensity. For example, for a 50 micron thick UV coating, if 70% of the UV energy is absorbed in the top 25 micron of coating, then 7% of the initial amount will be absorbed in the second 25 micron of coating

Amount of UV per unit area - Normally, the curing speed will increase with the amount of UV energy per unit area at the non-linear rate. If a 100 watt per cm^2 mercury lamp is increased to 200 watt per cm^2 , the curing speed would increase by tenfold. Furthermore, special metal halide lamps can trigger the receptor at an even faster rate with a standard 200 watt per inch lamp

Photo-crosslinkable acrylate or methacrylate oligomeric resins are used as based coats. By choosing a resin with the appropriate chemical structure, the mechanical properties of the UV cross linked resin can be modified. This includes brittleness and hardness. When optical properties are important, resins can be formulated to give specific refractive indices in the range of 1.44 to 1.6 (measured at 633nm). The UV resin is cured in a nitrogen atmosphere if oxygen inhibits the cross linking process. Mercury

UV source with an output power of 50-100 W/cm² is used to cure the resin. However UV power depends on type of resin used.

[Ahmed]

A typical composition of a UV –curable coating:

Resins (oligomers)	30-60 %
Reactive diluents (monomers)	5-50 %
Pigments, fillers, matting agents	0-40 %
Photoinitiators, synergist	2-15 %
Additives	1-5%

[Adhesives & Sealants Industry 2007]

3.1.1 Oligomers (radiation curable binders)

Customary used resins in UV-curing include the following classes:

- (1) unsaturated polyester/acrylated polyester,
- (2) acrylated epoxy resin,
- (3) acrylated urethanes (both aliphatic and aromatic),
- (4) acrylated silicone resins,
- (5) acrylated polyether,
- (6) acrylated melamines,
- (7) acrylated oils,
- (8) N-vinyl urethanes and
- (9) thiolene system

Acrylated polyesters

Polyester acrylates can be produced in a wide range of viscosities and reactivities to adapt to end uses in printing inks, wood and paper coatings. One of the major advantages offered by polyester acrylates over the other prepolymers is their low viscosity. As the molecular weight of the polyester decreases, its acrylated counterpart becomes more monomer like. One of the major problems associated with the use of the

low molecular weight polyester acrylates is the reduction in reactivity and the increased surface inhibition observed.

Acrylated urethanes

Reaction between hydroxyl and isocyanate groups proceeds efficiently at low temperature without the evolution of volatile by-products. The well known properties of urethanes, such as hardness, chemical resistance, toughness and light stability can be built into the acrylated, radiation curable prepolymers. The product is highly viscous and produces cured films which are very hard and inflexible but also highly chemical resistant. The poor colour properties are seen in the prepolymer as supplied, as well as in the relevant coatings (poor light and heat stability).

Acrylated silicones

Incorporation of silicone into radiation curable prepolymers is of interest in number of areas. Silicones are well known for their release properties, heat and water resistance. The advantages of silicone acrylates in the protection of optical fibres are afforded by their excellent flexibility and extensibility properties, particularly at low operating temperatures. At present state of development, silicone acrylates appear to be far more sensitive to air inhibition than other UV curable systems. Therefore curing under inert gas is often recommended.

[Shukla et al. 2004]

3.1.2 Diluents/monomers

As all the currently available oligomers (e.g. acrylated epoxy, acrylated urethane, etc.) are too viscous to be applied through conventional coating equipment, most formulators dilute the oligomer down to application viscosity. The diluents used to give system a workable viscosity have to be crosslinkable. A high level of monomer has to be added to obtain a low viscosity. However, earlier literatures indicated that to retain good reactivity in the mixture, as little monomer as possible should be used. As little monomer as possible should be added to a system, also for toxicological reason, to avoid skin irritation which is caused by a high level of monomer. It is obvious that, with a higher functionality monomer, the cure rate of the formulation will increase.

A monomer is selected for a system based upon its: photoresponse, contribution to the properties of the photopolymerised film properties, relative volatility, odour and toxicity, solvation efficiency and cost.

Vinyl based diluents styrene and its derivative such as methyl styrene and vinyl toluene: Styrene and its derivatives are of low cost, give good hardness and slow cure rate, are relatively volatile, but have good copolymerisation characteristics with many resins and other monomers. *Vinyl acetates:* Vinyl acetates are excellent reducers but are relatively volatile and flammable and also have poor weatherability and water resistance. [Shukla et al. 2004]

3.1. 3 Photoinitiators

The choice of photopolymerization initiator depends mainly on two factors: The solubility and its decomposition temperature. If the polymerization is performed in an organic solvent, then the initiator should be soluble in it and the decomposition temperature of the initiator must be at the boiling point or below of the boiling point of the solvent.

Photopolymerization initiators can be divided roughly into three groups with the generated active species; radicals, cations and anions. The conventional photopolymerization initiators generate free radicals upon light irradiation, and the resulting radical starts the polymerization process. Typical initiators are represented by benzoin derivatives. Photo-acid generators which produce cations (acid) by light irradiation were put to practical use in the late 1990s. Photo-base generators, which produce anions (base) by light irradiation, are of current interest in research. For a photopolymerization initiator to be an excellent initiator the following properties must be considered;

- High quantum yields in the generation of radicals, cations and anions
- Overlap in absorption wavelength of the photopolymerization initiators and emission wavelength of the light source
- High thermal stability and high stability in darkness
- Highly soluble in monomers and oligomers

[TCI America]

Initiating substances

Acrylic monomers do not absorb UV-light in a very efficient way and will not initiate radical polymerisation fast enough. As such, a photopolymerisable coating formulation essentially consists of a polymerisable vehicle (oligomer) and a light sensitive compound that is able to convert the absorbed light energy into a more useful form capable of causing the binder to polymerise into a hard solid mass. Such a light sensitive compound is known as a photoinitiator/ sensitizer. Thus, a photoinitiator is added which produces initiator radicals either directly by the fragmentation of the photo-excited state, or in two steps, by hydrogen transfer from a suitable substrate to the photo-excited state [Shukla et al. 2004]

Photoinitiators for radical polymerization are classified as cleavage (type I) and H-abstraction type (type II) initiators. The majority of type I photoinitiators are aromatic carbonyl compounds with appropriate substitution. For example, upon absorption of light, benzoin and derivatives, benzil ketals, acetophenones, aminoalkyl phenones, O-acyl-R-oximino ketones, R-hydroxyalkyl ketones, and acyphosphine oxides all spontaneously undergo “R-cleavage”, generating free radicals.

Because the initiation is based on a bimolecular reaction, the generation of free radicals from type II photoinitiators and curing rates is generally slower than the generation of free radicals from type I photoinitiators, which are based on unimolecular formation of radicals. These systems are, therefore, more sensitive to quenching of excited triplet states of the photoinitiators, which are the reactive precursors of light-induced chemical changes for carbonyl compounds. Indeed, quenching by monomers with low

triplet energy (e.g., styrene or N-vinylcarbazole) or by oxygen is often observed and may lead to relatively low curing rates when type I photoinitiators are employed.

[Yusuf, Steffen, Jockusch and Nicholas J. Turro 2010]

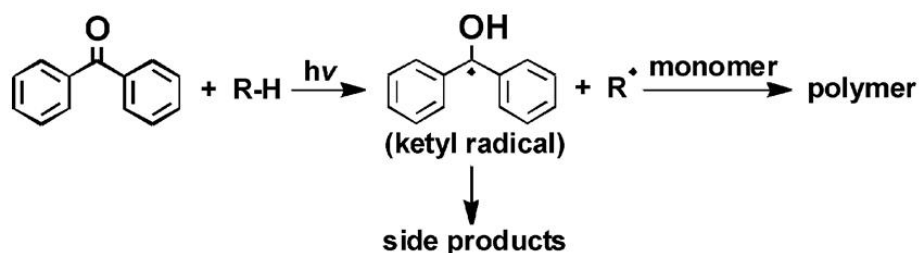


Figure 7: Type II Photoinitiation Mechanism with Benzophenone and Hydrogen Donors [Yusuf, Steffen, Jockusch and Nicholas J. Turro 2010]

Some common type of photoinitiators falls into the class of:

- aromatic ketones and synergistic amines
- alkyl benzoin ethers
- thioxathones and derivatives
- benzil ketals
- acylphosphine oxide
- ketoxime ester or acyloxime esters
- cationic curing quaternary ammonium salts
- acetophenone derivatives

[Shukla et al. 2004]

Although photoinitiators give the name to the whole process, the role that light plays in photopolymerization is restricted to the very first step, namely the absorption and generation of initiating species. Thus, in spite of its lowest volume in a polymerizable formulation, a photoinitiator plays a major role in the polymerization. A photoinitiator or photoinitiator system is defined as a molecule or combinations of molecules that, upon absorption of light, initiate the polymerization. [Bruce M. Monroe, Gregory C. Weed 1993]

In photocurable systems, photoinitiators affect mainly cure speed, yellowing, and cost. However, other factors such as commercial availability (or easy preparation), solubility particularly in a wide range of monomers, storage stability, and low migration, low odor, and nonyellowing properties in the cured films should also be taken into consideration. In addition, the light absorption properties of the selected photoinitiator need to match the emission wavelength of the light source. [Yusuf, Steffen, Jockusch and Nicholas J. Turro 2010]

Similar type II photoinitiator as a commercial application is manufactured by BASF. Formerly known as Ciba specialty chemicals, nowadays part of Company called BASF prepares series of photoinitiator chemicals with the name of IRGACURE[®].

IRGACURE 500 is a liquid mixture of two photoinitiators. It is used to initiate the photopolymerisation of chemically unsaturated prepolymers - e.g. acrylates - in combination with mono- or multifunctional monomers. IRGACURE 500 may be used after adequate testing alone or in combination with suitable co-initiators, such as amines for applications such as UV curable clear coatings for paper, metal and plastic materials.

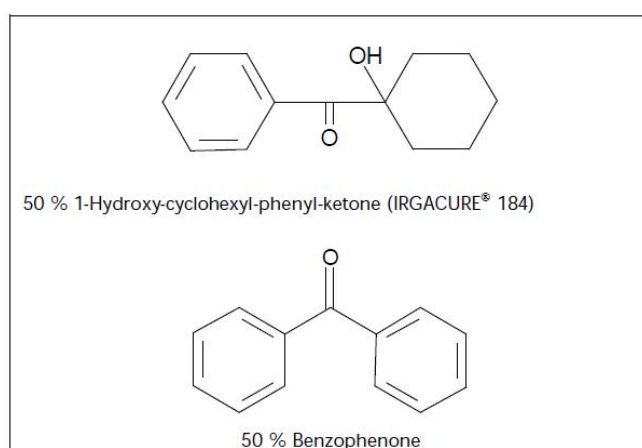


Figure 8: Chemical composition of IGRACURE 500

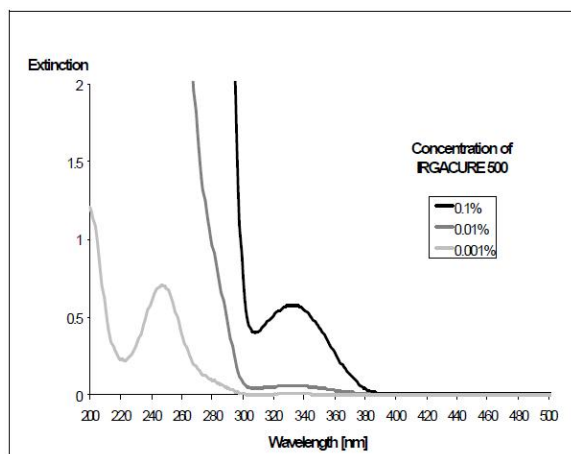


Figure 9: Absorption Spectrum of IRGACURE 500 (% in Acetonitrile)
[Ciba Specialty Chemicals Inc 2001]

4 Characterization of the UV-curing process

Determination of monomer reactivity is not always obvious or straightforward. Researchers rely on their experience and published data on individual monomers. In general, extent of conjugation in the molecular structure can be viewed as indicative of its tendency to form the initial free radical required for propagating a free radical polymerization. Usually, a more conjugated system is more likely to undergo the free radical polymerization. Beneath there is a scheme presenting the large variety of polymer networks having different architectures obtained by photoinitiated radical (R) or cationic systems (C).

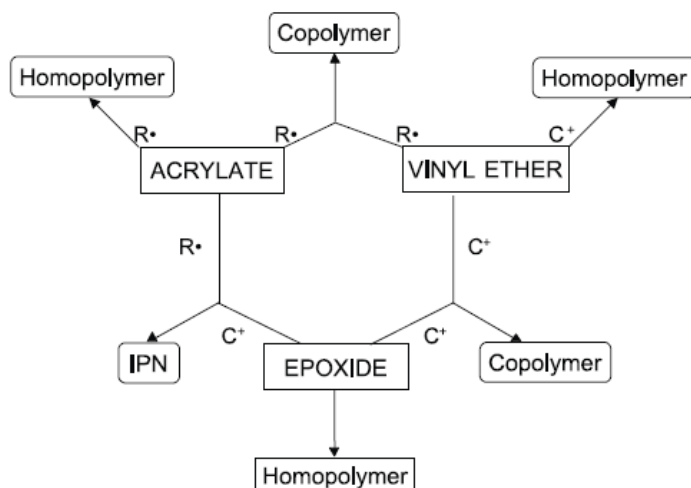


Figure 10: Synthesis of different types of polymer networks by photopolymerization of multifunctional monomers

IPN stands for interpenetrating polymer network. This kind of polymer network can lock one polymer network within another. [Decker 2001] This provides reinforcement, acoustic damping, impact resistance and restrains swelling in solvents. [Holme 2005]

4.1 Spectroscopic characterisation of the reaction kinetics

Radical chain polymerization usually includes highly reactive intermediates present at very low concentrations. Typical polymerization achieve a ready-state after a period that can be most a few seconds. That causes the inspection in real-time to be challenging.

The kinetics of the photopolymerization process has been evaluated by Fourier Transform Infrared Spectroscopy (FT-IR) simply by analysing sample before and after UV-irradiation and combining other variables with such UV irradiation time, quantity of the curable coating materials and surrounding processing conditions.

The curing mechanism is either radical polymerization for acrylate-based resins or cationic polymerization for epoxies and vinyl ethers. The properties of the UV-cured polymer matrix are determined by the cross-linking density. This depends on the type

and concentration of the photoinitiator and of the (optional) diluents, the intensity and the duration of the irradiation, and the temperature at which the curing process takes place. [Amerio et al. 2009] Such ultrafast reactions are easily followed in situ by real-time infrared spectroscopy, a technique that records directly conversion versus time curves.

4.1.1 Polymerization by NMR spectroscopy

In earlier study the degree of alkoxy silane condensation was monitored by solid-state ^{29}Si -NMR spectroscopy. Different structures are revealed by this technique. In this study investigation for hybrid organic-inorganic coatings was obtained by combining photopolymerization together with a sol-gel process (dual-curing process). Real-time FT-IR spectroscopy indicated that in all the systems a complete conversion of the photocurable reactive groups was achieved. Moreover the structure of the inorganic domains was studied by using ^{29}Si -NMR spectroscopy. These measurements indicated that both in methacrylic- and in epoxy-based systems indicating that for each Si atom, two or more alkoxy silane groups take part to the condensation reaction. [Amerio et al. 2009]

4.1.2 Polymerization by real-time FT-IR

FT-IR is in general use when investigating polymerization or other reaction kinetics. For example: Earlier study investigates the photochemical reactions of the modified polyols (compounds with multiple hydroxyl functional groups) by real time FTIR. By concentrating on certain bands, comparison of the spectrum before and after UV – irradiation tells about the reaction kinetics. For example, the hydrolysis of $\text{Si-OCH}_2\text{CH}_3$ groups to form Si-OH occur at 961 cm^{-1} , while other important reaction: the condensation of Si-OH groups to form Si-O-Si groups at 791 cm^{-1} . Band at 961 cm^{-1} is measured to overlap with Si-O stretching mode of Si-OH groups at 953 cm^{-1} , therefore the C-C-O in phase deformation band occurs at 791 cm^{-1} was used by J. Chen et al. to characterize the UV-reactivity the siloxane modified polyols. Consumption of $\text{Si-OCH}_2\text{CH}_3$ group at any time was calculated by studying the band at 791 cm^{-1} . Formula no.4. was used for calculating the conversion for the Si-OH groups to form Si-O-Si as time proceeds.

$$\text{Conversion}\% = \frac{[A_{(791\text{cm}^{-1})}]_0 - [A_{(791\text{cm}^{-1})}]_t}{[A_{(791\text{cm}^{-1})}]_0} \times 100 \% \quad (4)$$

where $[A_{(791\text{ cm}^{-1})}]_0$ and $[A_{(791\text{ cm}^{-1})}]_t$ represent the peak area under the 791 cm^{-1} band at the beginning of the reaction ($t = 0$) and at time t , respectively. The rate of polymerization R_p at time t then can be calculated by formula 5.

$$R_p = [M]_0 \frac{[A_{(791\text{cm}^{-1})}]_{t_1} - [A_{(791\text{cm}^{-1})}]_{t_2}}{t_1 - t_2} \quad (5)$$

where $[M]_0$ is the concentration of $\text{Si-OCH}_2\text{CH}_3$ groups at $t=0$. t_1 and t_2 represent reaction time at t_1 and t_2 , respectively. [Chen, Soucek 2003]

Another study evaluated the kinetics of photopolymerization process focusing on the methacrylic conversion. The methacrylic group conversion was evaluated by real time FT-IR. The methacrylic groups conversion was followed by monitoring the decrease in the absorbance of the band centred at 1640 cm^{-1} normalized with respect to the C=O band located at 1730 cm^{-1} . (*As far as cationic systems are concerned, the epoxy groups absorption at 970 cm^{-1} was considered and normalized to the ester band at 1670 cm^{-1} .*) [Amerio et al. 2009]

4.1.3 Polymerization by RAMAN spectroscopy

Raman spectroscopy is able to reveal the molecular composition of a sample at the micrometer scale in a non-destructive way. The information provided by the Raman spectrum of an oriented polymer differs from its infrared counterpart because of the fundamentally different processes involved in the generation of the spectra. In the

infrared absorption process, as already noted, the absorption intensity is dependent on the angle between the electric vector and the direction of the dipole moment change. The Raman spectrum results from inelastic photon scattering, details of which are determined by changes in the polarizability of the chemical bonds involved. Polarizability is a tensor quantity, which results in complications but, in principle, provides additional information. As we have seen, infrared spectroscopy involves only one beam of polarized radiation, and the fraction of the radiation absorbed by a molecule depends only on the orientation of the molecule with respect to the polarisation vector of the radiation. However, Raman scattering involves two beams of radiation, those of illumination and collection, and the scattered intensity depends on the orientation of the molecule with respect to the polarisation vectors of both beams, which may, of course, be different. This necessitates more detailed measurements in order to obtain the relevant information. [Fawcett 1996]

Literature offers good information about deformation and orientation measurements of polymers, less about the rate of polymerization measurements using Raman Spectroscopy

Raman spectroscopy is very effective in investigation of sol-gel precursors and materials derived from them. The technique is highly versatile with respect to excitation, detection and sampling possibilities. In addition, the presence of water does not hamper the measurement as it is the case of IR spectroscopy. When a Raman spectrometer is coupled to a confocal optical microscope, by means of which the laser is focused on the sample, Raman spectra can be obtained with a spatial depth resolution in the micrometer range. In many applications, micro-Raman spectroscopy has been shown to be a useful tool in the study of microprobe samples and films with thicknesses in the range of a few micrometers.

4.1.4 By X-Ray photoelectron spectroscopy (XPS)

XPS is also known as electron spectroscopy for chemical analysis (ESCA), is used to determine quantitative atomic composition and chemistry. XPS uses an X-ray beam to cause the emission of electrons from the surface of the sample. The electrons analysed do not have enough energy to escape from a depth of more than ~3-5 nm, so the XPS technique is inherently surface sensitive. The binding energy of the emitted electrons is

measured and used to identify the elements present. The thickness of surface layers and the depth distributions in the extreme surface region can be measured using angle-dependent XPS. By simply changing the angle of the sample to the detector, the effective depth of analysis can be varied in the range 1–10 nm.[Crompton]

XPS is a good technique for elemental analysis of solids and low vapour pressure liquids, with a detection limit to most elements of ~1000 ppm. It can be directly quantified; showing not only what is present, but also how much. This technique can be used to analyse polymers to a surface depth of 1–10 nm.

[Crompton]

- Surface analysis of organic and inorganic materials, stains, or residues
- Determining composition and chemical state information from surfaces
- Depth profiling for thin film composition
- Silicon oxynitride thickness and dose measurements
- Thin film oxide thickness measurements (SiO_2 , Al_2O_3 etc.)

EXPERIMENTAL

Confidential part of the report (pages 37-71, 76):

Following part of the thesis is concealed for 5 years for non-members of the PlasmaNice –project.

-Agreement on confidentiality was signed 21.9.2010

10 Sources

3DT LLC , PROCESS: HOW CORONA DISCHARGE WORKS [Homepage of 3DT LLC], [Online]. Available: <http://www.3dtllc.com/process.html> [2011, 1.18.] .

Adhesives & Sealants Industry 2007. UV/EB curable Systems. Adhesives & Sealants Industry, Jun 2007, Vol. 14, No. 6, pp. 20-22,24,26.

Ahmed, E.A. 2005. Italy calls for investigation of Nestlé's use of printing ink chemical. Food production daily news, Vol. packaging.

Ahmed, N. Roll to roll UV embossing technology. The Holography Times -Tech sheet, [Online], .

Amerio, E., Malucelli, G., Sangermano, M. & Priola, A. 2009. Nanostructured hybrid materials obtained by UV curing and sol-gel processes involving alkoxy silane groups. e-Polymers, 08 June 2009, , No. 059ISSN 1618-7229.

Arvanitoyannis, I.S. & Bosnea, L. 2004. Migration of Substances from Food Packaging Materials to Foods. Critical Reviews in Food Science and Nutrition, Vol. 44, No. 2, pp. 63-76. ISSN 1040-8398. doi: 10.1080/10408690490424621.

Brabec, C., Dyakonov, V. & Scherf, U. . Organic Photovoltaics - Materials, Device Physics, and Manufacturing Technologies. John Wiley & Sons. ISBN 978-3-527-31675-5.
http://www.knovel.com/web/portal/browse/display? EXT_KNOVEL_DISPLAY_bookid=3166.

Bruce M. Monroe, Gregory C. Weed 1993. Photoinitiators for free-radical-initiated photoimaging systems. Chemical Reviews, Jan 1993, Vol. 93, No. 1, pp. 435-448. doi: 10.1021/cr00017a019.

Bunshah, R.F. 1994. Handbook of Deposition Technologies for Films and Coatings - Science, Technology and Applications (2nd Edition). William Andrew Publishing/Noyes. 55-93 p. ISBN 978-0-8155-1337-7.
http://www.knovel.com/web/portal/browse/display? EXT_KNOVEL_DISPLAY_bookid=57.

Buschow, K.H.J., Cahn, R.W., Flemings, M.C., Ilshner, B., Kramer, E.J. & Mahajan, S. . Encyclopedia of Materials - Science and Technology, Volumes 1-11. Elsevier. 3576 p. ISBN 978-0-08-043152-9.
http://www.knovel.com/web/portal/browse/display? EXT_KNOVEL_DISPLAY_bookid=1871.

Chen, J. & Soucek, M.D. 2003. Photoinitiated cationic polymerization of cycloaliphatic epoxide with siloxane or alkoxy silane functionalized polyol coatings. European

Polymer Journal, 3, Vol. 39, No. 3, pp. 505-520. ISSN 0014-3057. doi: DOI: 10.1016/S0014-3057(02)00239-2.

Ciba Specialty Chemicals Inc 2001. Product data sheet:
Ciba® IRGACURE® 500
Photoinitiator. Edition: 4.9.2001, Basle ed. Ciba Specialty Chemicals Inc.

Crompton, T.R. . Characterisation of Polymers, Volume 1. Smithers Rapra Technology. ISBN 978-1-84735-122-7.

http://www.knovel.com/web/portal/browse/display? EXT_KNOVEL_DISPLAY_bookid=2221.

Decker, C. 2001. UV-radiation curing technology. Pigment & Resin technology, Vol. 30, No. 5, pp. 278-286. ISSN 0369-9420.

Fawcett, A., H. 1996. Fourier Transform Infrared and Raman Spectroscopies in the Study of Polymer Orientation. In: Anonymous Polymer spectroscopy. John Wiley & Sons. Pp. 176-177. ISBN 978-0-471-96029-4.

Han, Y., Taylor, A. & Mantle, M.D. and Knowles K. 2007. UV curing of organic–inorganic hybrid coating materials . Journal of Sol-Gel Science and Technology, Vol. 43, No. 1, pp. 111-123. doi: 10.1007/s10971-007-1544-8.

Holme, I. 2005. Novel coating and laminating technologies add value to products. Technical Textiles International : TTI, Vol. 14, No. 8, pp. 15-18,20.

Klein, L.C. 1988. Sol-Gel Technology for Thin Films, Fibers, Preforms, Electronics and Specialty Shapes. William Andrew Publishing/Noyes. 6 p. ISBN 978-0-8155-1154-0.
http://www.knovel.com/web/portal/browse/display? EXT_KNOVEL_DISPLAY_bookid=240.

MacKenzie, J.D. & BESCHER, E.P. 1998.
Structures, Properties and Potential Applications of Ormosils. Journal of Sol-Gel Science and Technology, Vol. 13, No. 1, pp. 371. ISSN 0928-0707.

Manmeet, K. & Srivastava, A.K. 2002. Journal of macromoleculr science, part C - Polymer reviews, Vol. 42, No. 4, pp. 481-512.

Martin, P.M. . Handbook of Deposition Technologies for Films and Coatings - Science, Applications and Technology (3rd Edition). William Andrew Publishing. ISBN 978-0-8155-2031-3.
http://www.knovel.com/web/portal/browse/display? EXT_KNOVEL_DISPLAY_bookid=3265.

Nanopost.com 2009.
Commerical Applications for Nanoscale Sol Gel Coatings. Quebec : electronics.ca
Publications: nanopost.com.

Pastorelli, S., Sanches-Silva, A., Cruz, J.M., Simoneau, C. & Paseiro Losada, P. 2008.
Study of the migration of benzophenone from printed paperboard packages to cakes

through different plastic films . European Food Research and Technology, Vol. 227, No. 6, pp. 1585-1590. ISSN 1438-2377.

Perking Elmer ltd.(ed.). 1994. The i-series FT-IR Microscope User's reference, Perking Elmer ltd. 152-153 p.

Rhodes, K., Valencia, M. & Bruner, S. 2007. Corona surface treatment and bonding with silicone adhesives. Adhesives & Sealants Industry, May, Vol. 14, No. 5, pp. 34-35. doi: 822978931.

Shukla, V., Baijpai, M., Singh, D.K., Singh, M. & Shukla, R. 2004. Review on basic chemistry of UV curing technology. Pigment & Resin technology, Vol. 33, No. 5, pp. 272-279.

Stowe, R.W. 2001. UV curing. Products finishing, 07/2001, Vol. 65, No. 10, pp. 4-5. ISSN 0032-9940.

TCI America, c. , *Product information* [Homepage of TCI America], [Online]. Available: <http://www.tciamerica.com/product/materials-chem/F013.shtml> [2010, 10.13.] .

Vossen, J.L. & Kern, W. . Thin Film Processes II. Elsevier. 502 p. ISBN 978-0-12-728251-0.
http://www.knovel.com/web/portal/browse/display? EXT_KNOVEL_DISPLAY_bookid=1708.

Watson, D.H. 2001. Food Chemical Safety, Volume 1 - Contaminants. Woodhead Publishing. ISBN 978-1-85573-462-3.
http://www.knovel.com/web/portal/browse/display? EXT_KNOVEL_DISPLAY_bookid=533.

Yusuf, Y. & Steffen, Jockusch and Nicholas J. Turro 2010. Photoinitiated Polymerization: Advances, Challenges, and Opportunities. Macromolecules, June 16, 2010, Vol. 43, No. 15, pp. 6245-6260. doi: 10.1021/ma1007545.