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Additives in Polymer Electronics

Daisuke Fujiki

6.1 Introduction

Ciba is global specialty chemicals company. The roots of Ciba date back to 1758 when J.R. Geigy Ltd., began trading in chemicals and dyes in Basel, Switzerland. In 1970, Geigy merged with Ciba - a Basel based chemical company founded in 1884 - to form Ciba Geigy Ltd.,. Ciba Geigy and the pharmaceutical company Sandoz merged in 1996 and formed one of the world's largest life science groups - Novartis. As a result of this merger, the specialty chemical division were spun off as Ciba Specialty Chemicals, Inc., in 1997. The company adopted the name Ciba, Inc in 2007. In April 2009, Ciba was acquired by BASF SE.

Ciba has three segments: Plastic Additives, Coating Effects and a Water and Paper. The Plastic Additives segment deals with colour and additives for plastics, lubricants and home & personal care. The Coating Effect segment is dedicated primarily towards the coating and imaging industries, while the Water and Paper segment provides solutions for paper and water treatment businesses.

6.2 Degradation and Stabilisation of Polymer

Many kinds of polymers are used in the electronics industries, from polyethylene to so-called super engineering plastics, such as polyethersulfone or polyimide. Almost all of them require additives. The reason for this is either to retain intrinsic characteristics or to extend those characteristics. In order to retain properties, polymers need process and heat stability, thermal stability or light stability. For the acquisition of new function, many kinds of functional additives can be added. Metal deactivators, antistatic agents and flame retardants are just some examples.

Each polymer has different degradation pattern and here shows representative degradation pattern of polyolefin, the so-called autoxidation cycle (Figure 6.1).

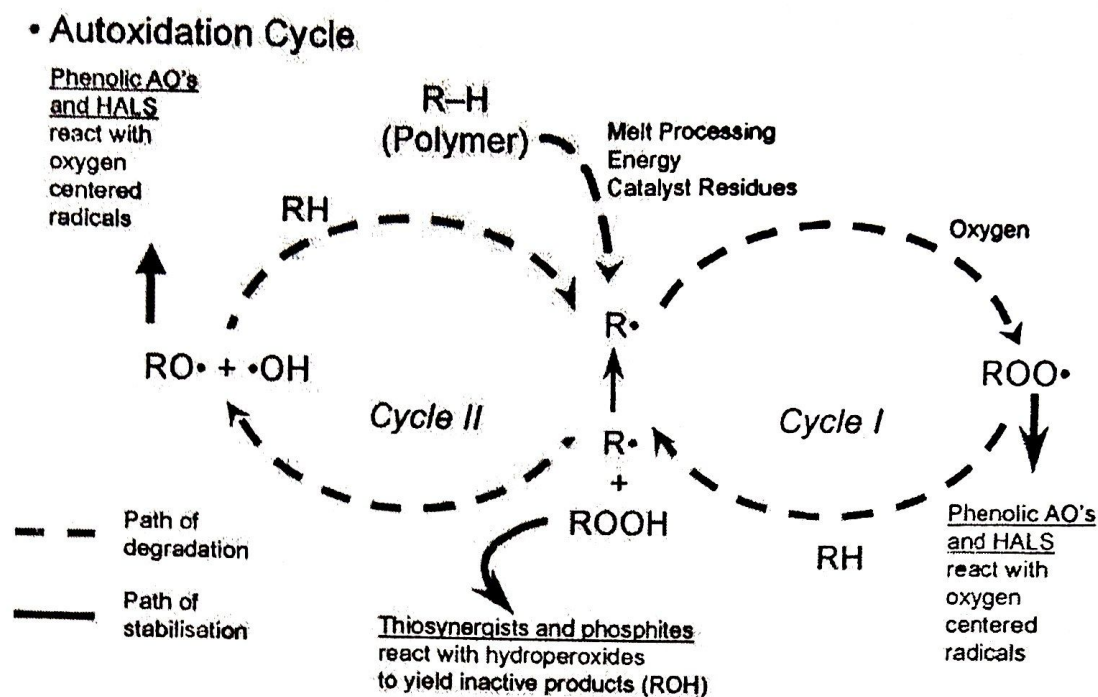


Figure 6.1 Degradation and stabilisation of polymer

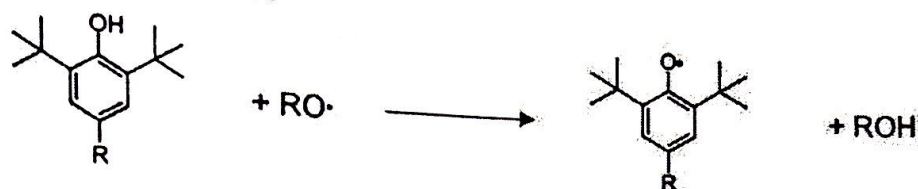
Polymer is degraded by heat, energy, UV or residues of catalyst and generates alkyl radicals. This alkyl radical reacts with oxygen and form peroxy radicals. These peroxy radicals abstract hydrogen from other polymer and forms alkyl radicals and hydroperoxide. The decomposition of hydroperoxide to alkoxy and hydroxyl radicals induces additional decomposition of the polymer chain. In order to stop the radical chain reaction of degradation, stabilisers such as phenolic antioxidant, phosphites, thioether and hindered amine light stabilisers (HALS) are added.

Figure 6.2 shows some representative processes for degradation and stabilisation of polymers. Phenolic antioxidants react with peroxy radical and alkoxy radical by donation of hydrogen. Phosphites and thioether act as reducing agent for hydroperoxide, which is converted to alcohol. Hydroxylamine, which is a relatively new stabiliser, acts as hydrogen donor and hydroperoxide decomposer.)

As illustrated in Figure 6.3, there are two kind of light stabilisers, HALS and UV absorbers. HALS react with alkyl radicals and peroxy radicals after activation by oxygen and light. The radical stabilisation reaction should be cycled as shown.

UV absorbers absorb harmful light and the absorbed energy is converted to harmless heat. The absorbance of UV absorbers depends on the sample thickness and concentration. This law is called Beer-Lambert law.

- Hindered phenol



- Phosphite



- Thioether (Thiosynergists)



- Hydroxylamine (phenol free)

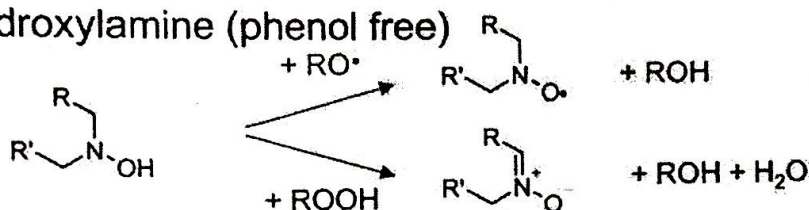
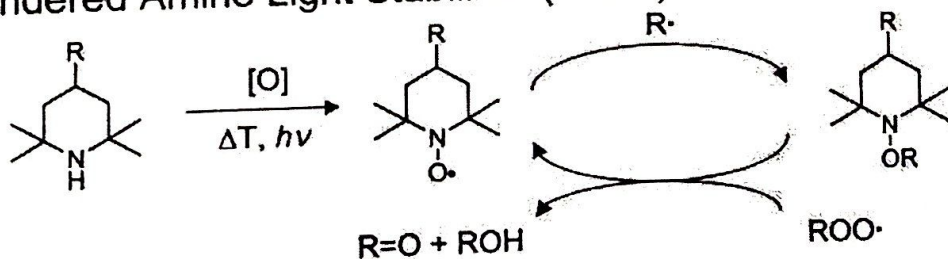


Figure 6.2 Process and heat stabilisers

- Hindered Amine Light Stabilizer (HALS)



- UV absorber

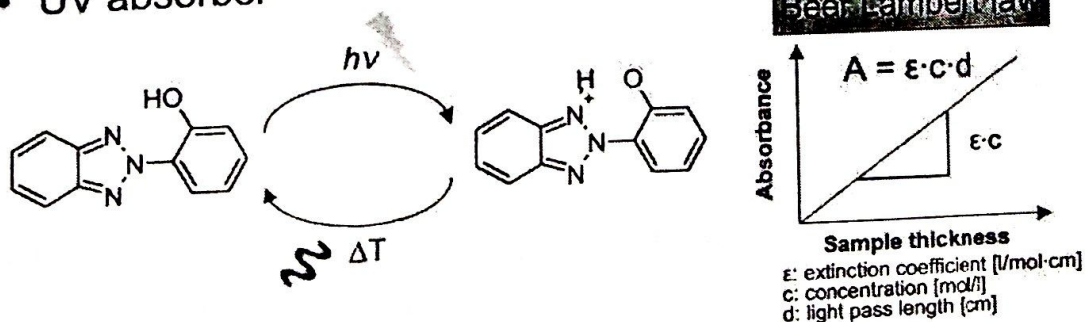


Figure 6.3 Light and heat stabilisers

Table 6.1 Harmful wavelength for polymers				
Wavelength λ and hemolytic bond dissociation energy E ($AB \rightarrow A\bullet + B\bullet$) of some organic molecules				
	λ , nm	Bond	Bond type	Bond energy, kJ/mol
UV-B	230	$-C-C-$	aromatic	520
	290-310	$R-O-H$	alcohol	420-385
	290	$R-CR_2-H$	prim / sec / tert H	410 / 395 / 385
	320	$-C-O-$	ether	365-390
UV-A	240	$R-CH_2-CH_2$	aliphatic	335-370
	350	CR_2-Cl	aliphatic chloride	330-350
	360	CH_2-NR_2	amine	330
	400	$-O-O-$	peroxide	270
<i>prim: primary, sec: secondary, tert: tertiary</i>				

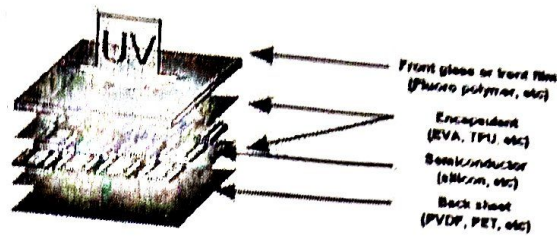
Table 6.1 shows the wavelength that specific bond absorbs, which leads to the decomposition of the bond. For example, the ether bond absorbs at 320 nm wavelength and amine absorbs at 360 nm wavelength. This means the UV absorber should absorb those corresponding wavelengths of light in order to protect the polymer against UV radiation.

6.3 Stabilisers for Polymer Electronics

Normally UV comes from the sun. The polymers for outdoor applications; here is an example of photovoltaic module, need protection against UV radiation (Figure 6.4). In electrical and electronics applications, not only the sun but also the light can be the source of the UV radiation. For example, the modules in liquid crystal display (LCD) also need to be protected against UV radiation emitted by the back light. The fluorescent light possess specific sharp emission of UV radiation and the materials need protection against it.

For UV management, proper understanding for UV absorbers is necessary. Most UV absorbers, independent on the type of chromophor, absorb the damaging light and emit non destructive heat. This is the examples of benzotriazole type of UV absorbers (Figure 6.5). In the market, different kinds of substitution of benzotriazole UV absorbers are

- UV irradiation by sun
 - Outdoor applications



- UV emission by light
 - Indoor applications

- Lighting
- Display

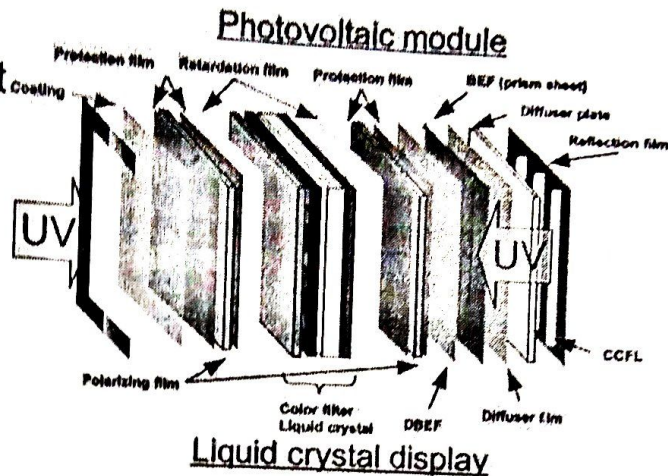
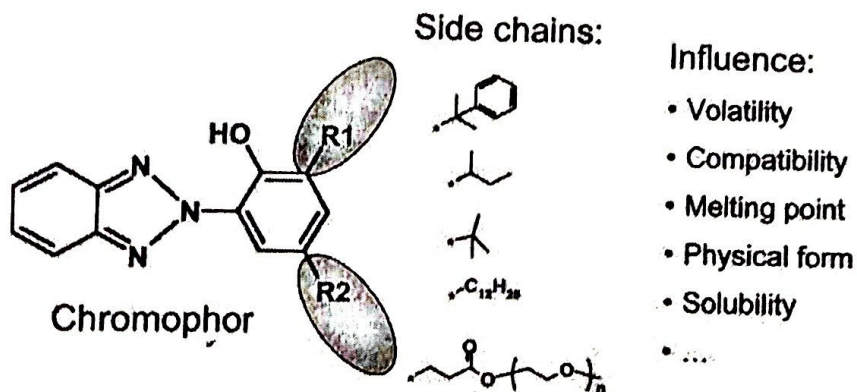


Figure 6.4 UV management in polymer electronics



The right UV absorber for the right application

Figure 6.5 Side chain effect on benzotriazole UV absorbers

Figure 6.6 TGA of benzotriazole UV absorbers

available. The reason is different side chains provide different physical influence, such as volatility, compatibility to the polymer, melting point and others. One example is thermal gravity analysis (TGA) of UV absorbers (Figure 6.6). All of the UV absorber have benzotriazole chromophor but different substitutions. This gives molecules of differing molecular weight. Consequently, they also then have different volatilities. If the processing temperature is quite high, low volatility UV absorbers should be used.

6.4 Functional Additives for Polymer Electronics

So far the retention or stabilisation of polymer characteristics has been discussed. The last part is functional additives in polymer electronics. In electronics applications, polymer tends to have contact with metals because metals are used as conductors, solder, springs, screws and other small parts. If the polymer is in contact with metals, especially transition metals, the degradation of polymer is accelerated. In that case, metal deactivation provides the solution. ✓

Standard application of metal deactivator is jacketing of the cable because it contacts to copper wire. Copper ions can accelerate the degradation by changing valance.

Metal deactivators act as electron donors to form a stable complex with copper ions and the degradation reaction is retarded. Here is an example of adding 0.2% copper ion and with/without 0.2% IRGANOX® MD 1024 (Figure 6.9). IRGANOX® MD 1024 helps to retain the mechanical properties.

- Metal ion catalyze the degradation of polymer
 - Especially transition metal ions: low energy to change the valence state
 - Cu, Fe, Co, Mn, Ce and V
- Metal deactivators form stable complexes with metal ions
 - Degradation of polymer is also retarded

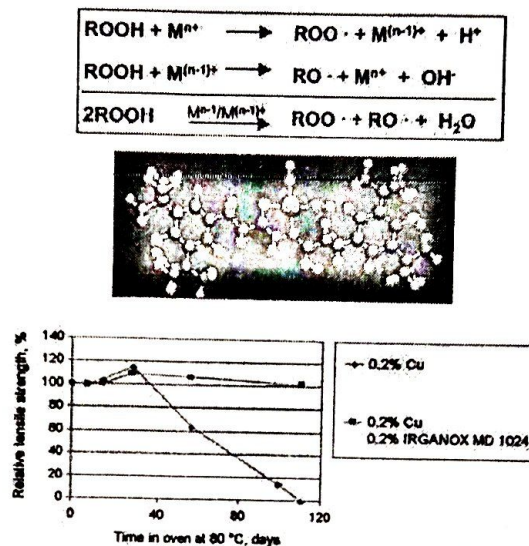


Figure 6.9 Function of metal deactivator

Electricity induces static charge. This causes dust pick up, which interferes with the clarity, handling problems and electrical discharges which may induce electrical shocks for fire or dust explosion. Antistatic agents can solve such an issue.

Classical antistatic agents such as glycerine mono-stearate or amines migrate to the surface of the polymer and anchor in the polymer while the polar groups project out of polymer. The polar groups absorb the humidity in the air and form a conductive path at the surface. The drawbacks are performance over time, thermal stability, humidity dependency and migration itself, which causes the stickiness of the film. On the other hand, the discharging mechanism of IRGASTAT® is to build a conductive network in the polymer matrix and release the charge (Figure 6.10). The performance is not affected by humidity and the performance lasts a long time until the network breaks. The benefits are to minimise the risk of fire or explosion and damage to the product by electrostatic discharge during handling or transportation, on top of dust pick-up.

MELAPUR® 200 yields UL94 V-0 for GF-PA

- Mode of action

- Heat: endothermic decomposition of melamine and phosphoric acid, resulting in heat sink
- Oxygen: phosphoric acid forms char layer, preventing mixing of oxygen and combustible gases
- Fuel: melamine acts as blowing agent, increasing thickness of char layer, which then insulates polymer from heat

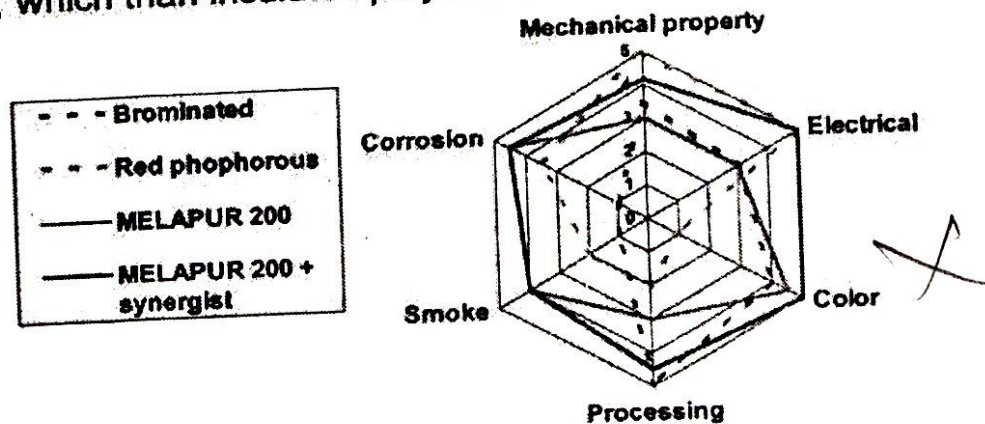


Figure 6.10 Advantages of MELAPUR® 200

The last topic is halogen free flame retardants. Needless to say, the benefit of flame retardancy is to minimise the risk of fire accidents. Melamine derivatives are a niche in the flame retardant market, but have significant advantages in specific polymers.