APPLICATION NOTE

ANE018 | Plastic Material Properties

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01. INTRODUCTION

It has been observed that the natural color of halogen-free polyamide (PA) plastic used in Würth Elektronik connectors turns brown during the SMT process (Reflow soldering). The aim of this technical note is to understand this phenomenon and demonstrate whether and how it may impact the plastic material properties of our connectors. This was achieved by conducting spectroscopy IR and differential scanning calorimetry tests.

02. PHENOMENON/EXPLANATION

Halogen-free polyamides are a group of polymers that are characterized by a repeating amide bond (Figure 1). Polyphthalamide (PPA) ranks among the high performance polymers. The repeating unit in the polymer chain is composed of a combination of terephthalic (aromatic) and methylendiamine: PAnT [1].

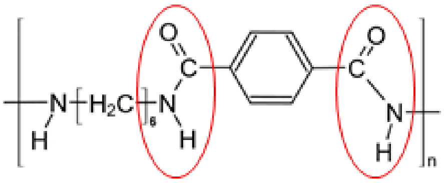

Figure 1: *Example of a polyamide. Note the amide groups circled in red.*

The color change is a consequence of the thermos-oxidation when the product is exposed to high temperature in an oxygen environment (initiation phase). This is characteristic of halogen-free PA materials of natural color. The degradation process depends on the nature and the structure of the macromolecular chain, as well as on the chemical nature of the branched groups. As regards to polyamides, oxidation occurs by hydroperoxides (ROOH) within a short-chain mechanism.

The thermo-oxidation of a hydrocarbon polymer results from the extraction of an H atom because of temperature. The resulting radical (R▪) reacts very quickly with the oxygen (O_2) available to form a peroxy radical (ROO▪). During the reaction process, the ROO▪ strips the hydrogen atom from a methylene (RH) and forms a hydroperoxide (ROOH). The hydroperoxide (ROOH) comes along with a radical (R▪) and thus propagates the chain reaction process (Figure 2). This is greatly accelerated at higher temperatures.

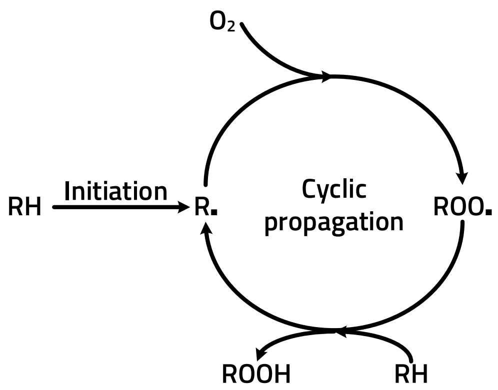

Figure 2: *Cyclic propagation of ROOH hydroperoxides.*

Oxygen absorption starts after a certain time (induction time). It is followed by an accelerated rise in concentration of the peroxy groups. When the peak is reached (autocatalytic stage), this is followed by the depletion of peroxy groups (termination stage). The temperature and diffusion coefficient of oxygen determines the rate of the oxygen absorption while the induction time depends on the polymer nature, structure and density. The oxygen absorption is also proportional to the polymer open surface.

The absorbed oxygen mass in the thermal oxidation process is inversely proportional to the crystallinity degree of the polymer. The oxidation process starts within its amorphous phase or interfibrilar areas. A branched polymer offers less resistance to oxidation than a linear polymer.

03. TESTS RESULTS

In order to observe this phenomenon, we tested the behavior of two polyamide products under reflow soldering at 260 °C. The plastic surface of the housing turns brown (Figure 3 and Figure 4).

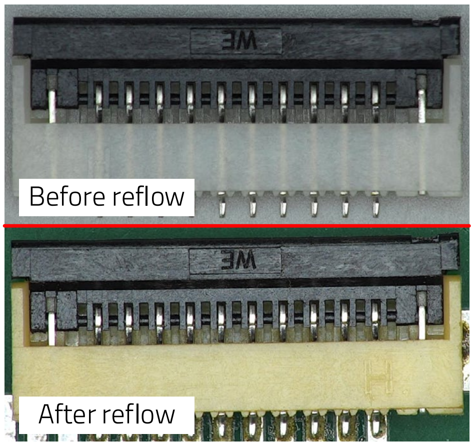

Figure 3 : *ZIF connector 6861xx148922 before and after reflow*

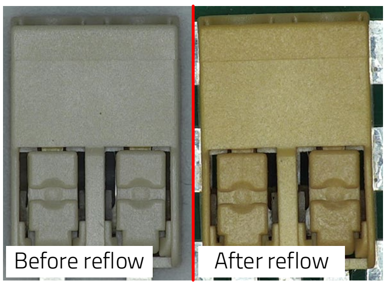

Figure 4 : *LECO Connector 695402400222 before and after reflow*

3.1 Contact resistance analysis

Contact resistance measurements carried out after reflow soldering indicated that they comply with the values stated in the technical data sheets (Table 1), i.e. less than 50 mΩ per contact depending on the products.

Matchcode	Series	CR/pin in datasheet (mΩ)	CR/pin after reflow soldering (mΩ)
WR-FPC	6861xx14892x	< 50	40
WR-FPC	6871xx14902x	< 50	30
WR-FPC	6861xx183822	< 30	19
WR-LECO	6954xx150122	< 20	16
WR-LECO	6954xx151122	< 20	16
WR-LECO	695401000222	< 10	2

Table 1: Contact resistance of connectors stated in the data sheet and measured after reflow.

3.2 Amide group analysis

In order to identify the surface oxidation phenomenon, our affected products were tested by spectroscopy before and after the reflow 260 °C process of a ZIF connector 6861xx148922 (PA6T) (Figure 5) and LECO connector 695402400222 (PA9T) (Figure 6). Spectroscopy is a fundamental exploratory tool in the field of physical chemistry that enables the identification of the elements and compounds of materials.

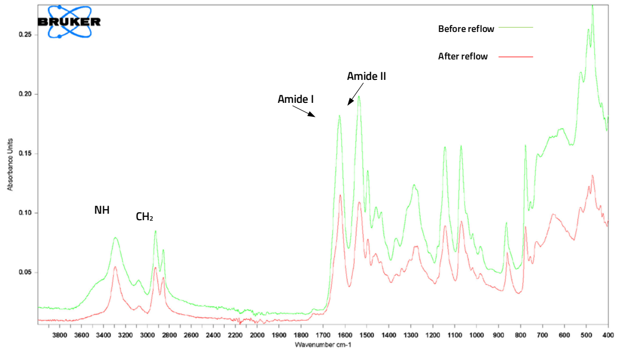

Figure 5 : *Spectroscopic analysis of amide functional groups (ZIF – PA6T)*

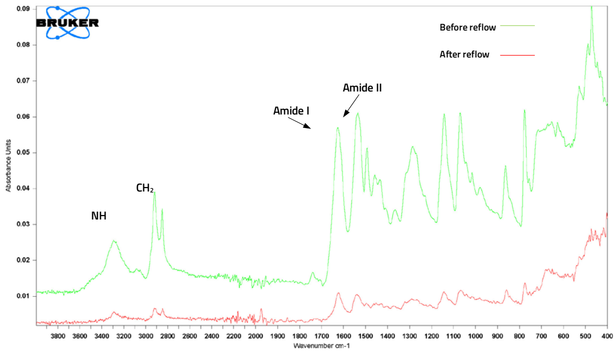

Figure 6 : *Spectroscopic analysis of amide functional groups (LECO – PA9T)*

The position of the peaks shows no difference before and after reflow. As a conclusion, the color browning neither altered the plastic material composition or structure, and therefore its properties. However, looking at each material independently, there is too much interference between the groups to interpret the absorbance rate before and after reflow. To interpret the graph, the importance is the position of the peaks (absorption wavelength) and not their heights (absorption value).

3.3 Phase change analysis of polyamides

Differential Scanning Calorimetry (DSC) is a plastic material characterization method. DSC is a thermal analysis technique used to measure the differences in heat exchanges between the analyzed sample and a reference product during a physical transformation, such as the glass transition temperature (the material changes from a glassy, solid, rigid state a rubbery state) represented by the green curve of the thermogram, and the melting temperature (the material moves from solid to liquid) represented by the red curve of the thermogram.

3.4 Melting Point

When conducting the DSC tests, the melting temperature for the samples were also recorded. Three measurements were taken for each part: an initial sample without any previous heating process, a sample after a 260 °C reflow profile and a sample after a 260 °C DSC profile under a N_2 atmosphere, which simulates the reflow profile without oxygen.

We could observe the melting point under the second phase (red curve of the thermogram), which corresponds to the rubbery state and reaches the melting point (passage from solid state to liquid state).

When the temperature drops, the sample becomes more rubbery (blue curve) then solid again (khaki curve).

6861xx148922: for PA6T, the theoretical value is 295 °C.

Initial samples (Figure 7)	Peak = 310.1°C
Samples after reflow 260°C (Figure 8)	Peak = 311.6°C
Samples after DSC 260°C (Figure 9)	Peak = 307.8°C

Table 2 : Measured Peak – ZIF 6861xx148922

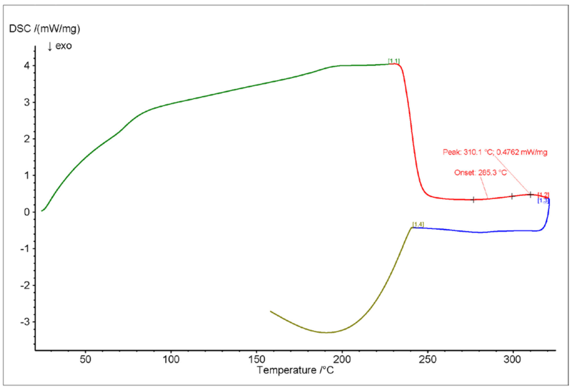

Figure 7 *: ZIF initial*

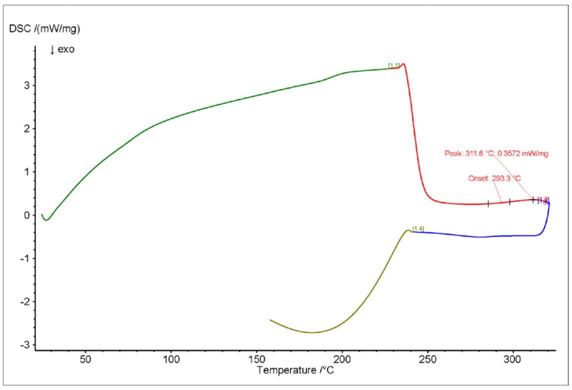

Figure 8 *: ZIF after reflow 260°C*

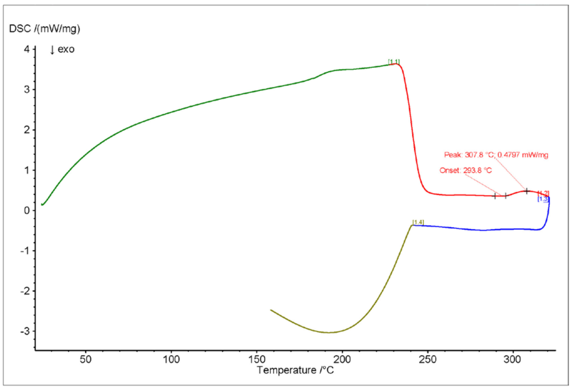

Figure 9 *: ZIF after DSC 260°C*

695402400222: for PA9T, the theoretical value is 305°C.

Initial samples (Figure 10)	Peak 1 = 278.2°C Peak 2 = 300.1°C
Samples after reflow 260°C (Figure 11)	Peak 1 = 276.9°C Peak 2 = 298.7°C
Samples after DSC 260°C (Figure 12)	Peak 1 = 277.8°C Peak 2 = 307.7°C

Table 3 : Thermograms show two melting temperature peaks, which is characteristic of PA9T

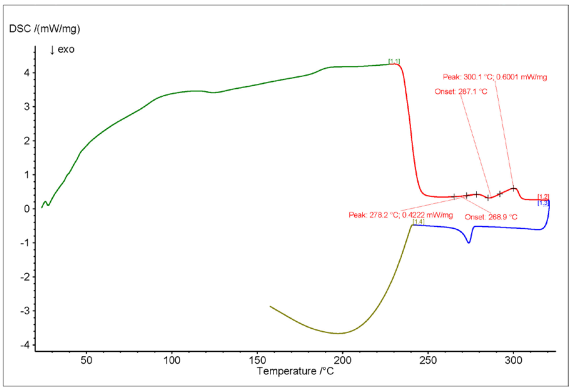

Figure 10 : *LECO initial*

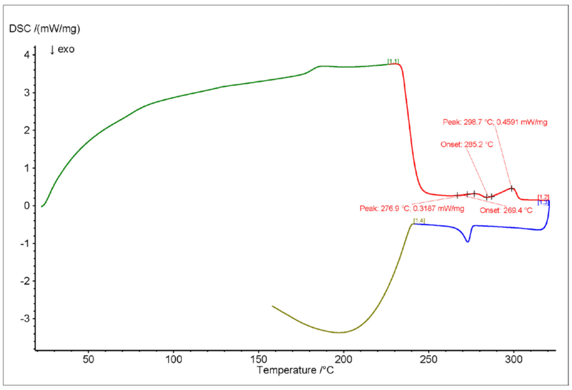

Figure 11 : *LECO after reflow 260 °C*

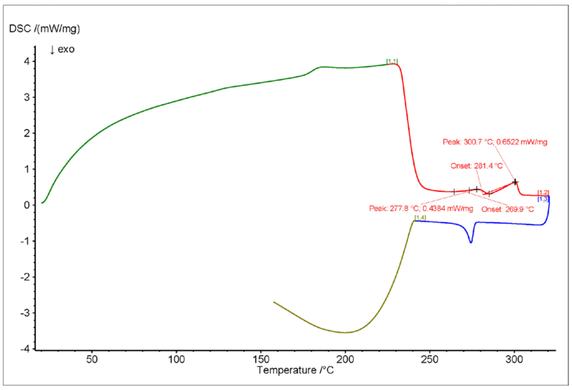

Figure 12 : *LECO after DSC 260 °C*

On each of these curves, the melting temperature remains the same before and after soldering processes. This means that heating processes do not cause any change in material or any damage of the plastic material.

3.5 Surface Oxidation

In order to prevent the surface oxidation of a halogen-free polyamide material, there must be no oxygen present when exposed to high temperature. Reflow oven conditions without the presence of oxygen were simulated using the DSC test equipment. As opposed to the reflow atmosphere, DSC analyses are performed with an inert gas (nitrogen) atmosphere in order to prevent any material reaction with the atmosphere.

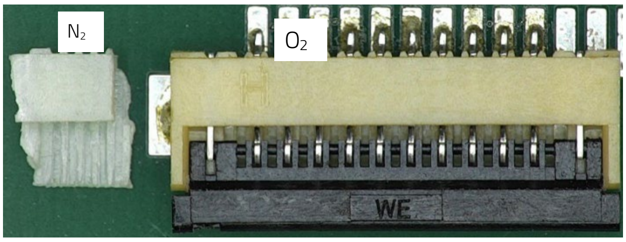

Figure 13 : *On the left, a portion of a ZIF 6861xx148922 heated in the DSC to 260 °C with Nitrogen (N_2) vs. Reflow at 260 °C with O_2*

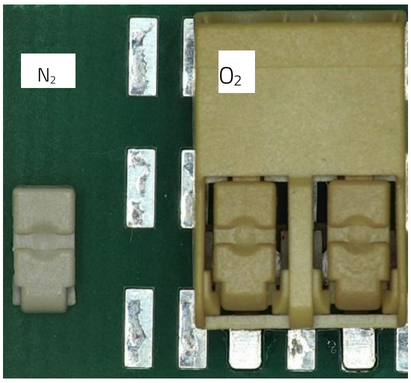

Figure 14 : *On the left, a portion of a LECO 695402400222 heated in the DSC to 260 °C with Nitrogen (N_2) vs. Reflow at 260 °C with O_2*

We can observe that a nitrogen atmosphere prevents the surface oxidation of the plastic material during high temperature processes.

04. CONCLUSION

Halogen-free PA of natural color turns brown when exposed to high temperature in an oxygen atmosphere in order to solder connectors on printed circuits when using reflow soldering, for example. However, the tests conducted confirm that the solder joints, as well as the plastic properties, remain compliant. Only the top layer of the polymer has absorbed oxygen which is only an aesthetic change but it does not impact the product specifications, performance or behavior. Indeed, spectroscopic and DSC tests do not show any change in the physical or molecular structure of the plastic after the soldering process.

In addition, this surface oxidation phenomenon has been taken into account during the product design and qualification. Our electrical and mechanical tests were conducted after soldering of the connectors on printed circuits, that is, after the surface oxidation phenomenon, and under operating conditions of the customer applications. The successful test results demonstrate that the products remain compliant even with the color browning. If the aesthetic of the product is important to the design, surface oxidation can be prevented by performing the reflow soldering process under a nitrogen atmosphere.

This note is not relevant for white colored and halogenated PA plastic products.

05. BOM

Matchcode	Series	Description	Plastic Material
WR-FPC	6861xx14892x	1mm ZIF SMT Horizontal Hinge type Bottom Contact	PA6T
WR-FPC	6871xx14902x	0.5mm ZIF SMT Horizontal Hinge type Bottom Contact	PA6T
WR-FPC	6861xx183822	1mm ZIF SMT Vertical Type A	PA6T
WR-LECO	6954xx150122	1.50mm LECO SMT Horizontal Plug	PA6T
WR-LECO	6954xx151122	1.50mm LECO SMT Horizontal Receptacle	PA6T
WR-LECO	695401000222	LECO SMT Vertical 1 pin poke-in	PA9T
WR-WTB	6531xx124022	1.25mm WTB SMT Male Vertical Shrouded Header	PA9T

A.1 References

[1] Sorin ILIE; Radu SENETSCU/TE-VSC/Cern/Polymeric Materials Review on Oxidation, Stabilization and Evaluation using CL and DSC Methods

IMPORTANT NOTICE

USEFUL LINKS

Application Notes
www.we-online.com/appnotes

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www.we-online.com/redexpert

Toolbox
www.we-online.com/toolbox

Product Catalog
www.we-online.com/products

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