International Journal of Engineering Science Invention
ISSN (Online): 2319 – 6734, ISSN (Print): 2319 – 6726
www.ijesi.org ||Volume 5 Issue 12|| December 2016 || PP.27-33

Analysis of the Change in Curing Temperatures as a Result of Hydrolysis of Electrostatic Thermosetting Powder Coating Residue

Yilmaz KISMET[1]
[1](Department of Mechanical Engineering, Munzur University, Turkey)

ABSTRACT ***:*** *Changes in thermal properties of electrostatic thermosetting powder coating residue (polyester/epoxy and polyester/polyurethane) and hydrolyzed form of these residues were analyzed by "Differential Scanning Calorimetry" (DSC) and "Kofler Hot Bench" in the present study. Glass transition, melting, and crystallization temperatures of two different electrostatic thermosetting powder coating residue were measured with DSC analyses to determine the effects of hydrolysis. Melting and curing (hardening) temperatures were determined using kofler hot bench experiment, a simple and fast method. As a result, it was observed that, while the temperature that the thermosetting powder coating residue started to create film coating on metal surfaces was approximately 130°C, it commenced to increase to 160°C in certain residue, and up to 190°C in others with hydrolysis. Thus, it would be possible to utilize electrostatic thermosetting powder coating residue in high temperature manufacturing applications in the polymer industry (extrusion manufacturing, hot pressing, injection molding, blow molding, etc.).*

KEYWORDS – *DSC, hydrolysis, kofler hot bench, powder coating, recycling.*

I. INTRODUCTION

Electrostatic powder coating technology that has a history of approximately 60 years is used not only in coating of metal material, but also in coating aluminum and polymer, and several other materials for decorative purposes today [1-4]. Powder coating does not contain solvents as opposed to wet paint. Since it contains no solvent, harmful gas emissions were not released during powder coating applications [1,3]. It is preferred more in the developed technology environment of today with its high productivity, low energy costs and environment friendly properties and it is becoming more prevalent [2,5].

There are two different types of powder coating, namely thermosetting and thermoplastic, which are obtained by mixing specific proportions of resin, hardener, pigments, filling material, and additives [1,3,8]. Powder coatings that include 80% resin and hardener by weight are also named based on the resin and hardener they contain [1,2]. These materials that form powder coating initially weighed according to the rates required by the desired compound and mechanically mixed in a pre-mixer. To ensure the homogeneity of the mixture, it is processed in the extruder under certain temperatures depending on the type of powder coating. The material that turns into melt in the extruder is initially cooled at the extruder exit and then broken into chips sized pieces. Finally, these pieces are pulverized in a grinder or a mill to obtain the powder [1,3,11].

Before the material is coated with powder coating, the surfaces are cleaned with mechanical or chemical techniques. Afterwards, powder coating is sprayed onto these surfaces using a spray gun. Powder coating is charged in spray guns using two different methods of “tribo” or “corona” charging. In both methods the material that would be coated is grounded. In corona technique, powder coating is negatively charged with electron donation while passing through the gun, while powder loses electrons due to friction while it passes through the gun due to the propertied of the gun becoming positively charged in tribo method. In tribo method, grounded material obtains the electrons from the ground towards the powder particles and is charged negatively. In corona, due to grounding the electrons flow towards the ground and the material that needs to be coated is charged positively. In both cases, an electrostatic gravitation occurs between the powder particles and the material to be coated enables the adsorption of powder coating particles to the material surface [1,9]. Later on the material were cured under certain temperatures and durations based on the properties of the electrostatic powder coating used. Usually firing temperatures vary between 130 and 240°C for thermosetting powder coating, while the materials are cured under higher temperatures, between 300 and 400°C for thermoplastic powder coating [6,7,10-13].

Since energy costs would increase as a result of the higher firing temperatures, industries prefer thermosetting powder coating, which requires lower firing temperatures, and 90% of total paint production in the industry is thermosetting powder coating. Firing duration which varies between 5 to 30 minutes is important as well as the firing temperature for powder coating. With the appropriate firing temperature and duration a film coating of the desired thickness, resistant to corrosion is obtained on the material surface that does not contain any solvent [14,23].

During spraying, powder particles that were not charged could not adhere to the material and hence fall to the ground. Thus, one third of powder coating used in small and mid-size businesses during each process is lost. It is possible to reuse these losses but only with low productivity and the loss amount increases on the second run, reaching over 50%. Losses are reduced to 5% in mass production units using conveyor systems [1,3].

Thermal properties of electrostatic powder coating residue and hydrolyzed version of these residues that have over 2 million tons of production potential throughout the world per year were scrutinized in the present study and the variations on these thermal properties as a result of hydrolysis were identified. Instead of reusing the powder coating residue as coating material under high temperatures, the study aims to peruse these materials using different production techniques such as extrusion, injection molding and hot pressing.

II. EXPERIMENTAL

Material used in the study is detailed in Table 1. As could be observed in the table, two different electrostatic thermosetting powder coating residues and the products obtained via the hydrolysis* of these residues were used in the analyses.

Table I: Thermosetting powder coating residue used in the analyses and the systems they belong to

Residue Material	Resin	Hardener	System	Color
Hybrid System (EP-SP and EP)	Polyester/Epoxy	Epoxy	Termosetting	Black
Polyester-Polyurethane (SP-PUR)	Polyester	Isocyanatadduct	Termosetting	White

The first kind of powder coating depicted in Table 1 is the compound of two similar powder coating systems of a hybrid system of carboxyl group bound polyester and epoxy hardener (EP – SP) and a dark colored structure with epoxy resin and hardener (EP). The second type of powder coating was a white powder coating with a hydroxyl group bound polyester resin and polyurethane (SP – PUR) based isocyanate duct hardener.

2.1 THERMAL ANALYSES

Differential Scanning Calorimetry (DSC) analyses were conducted for two different electrostatic thermosetting powder coating residues given in Table 1 before and after hydrolysis. Furthermore, curing temperatures of residues were determined using Kofler hot bench and their adhesion properties to metal surfaces were rapidly and simply identified. The reactions given by the hydrolyzed and non-hydrolyzed residues based on the increase in temperature were observed and interpreted using the results obtained via the above mentioned processes.

2.1.1 DSC ANALYSES

DSC analysis for the residue mentioned in Table 1 and their hydrolyzed forms were conducted using Mettler Toledo DSC 822 equipment in Berlin Technical University Polymer Institute laboratories. For these analyses, 5 - 10 mg samples were prepared. Later on, these samples were heated from 20^{o}C to 240^{o}C with a 10^{o}C /min increment, and then cooled with the same increment rate (10^{o}C /min). Samples were heated and cooled twice consequently for each analysis [1,4,15-21].

2.1.2 KOFLER HIT BENCH

The residues referenced in Table 1 and their hydrolyzed forms were analyzed by heating with the Kofler hot bench shown in Figure 1. Thus, the temperatures that the material started to form a film coating on metal surfaces after melting were identified.

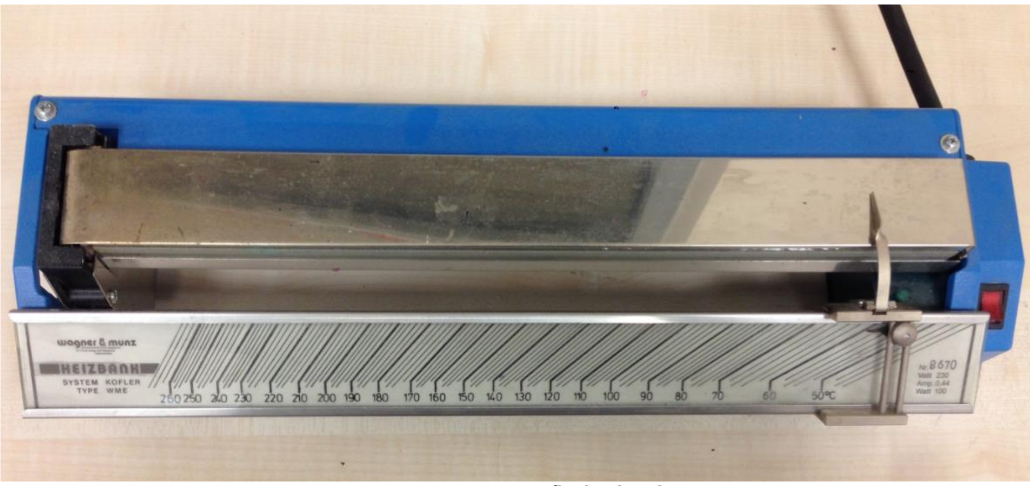

Figure 1: Kofler hot bench

20 mg samples were weighed and flattened on aluminum foils. Later on these foils were placed on the hot bench shown in Figure 1, with a heating internals of 50 to 260oC, and heated for 10 minutes. Following the heating process, the samples were taken from the hot bench and left for cooling for a few minutes. Thus, the variations of the temperatures required for adhesion of the residues on metal surfaces with hydrolysis were determined.

III. RESULTS AND DISCUSSION

3.1 DSC RESULTS

The residues referenced in Table 1 were heated from 20 to 240oC with a speed up rate of 10K per minute and cooled with the same rate. This process was repeated twice for each sample and the results are presented in the graphs below.

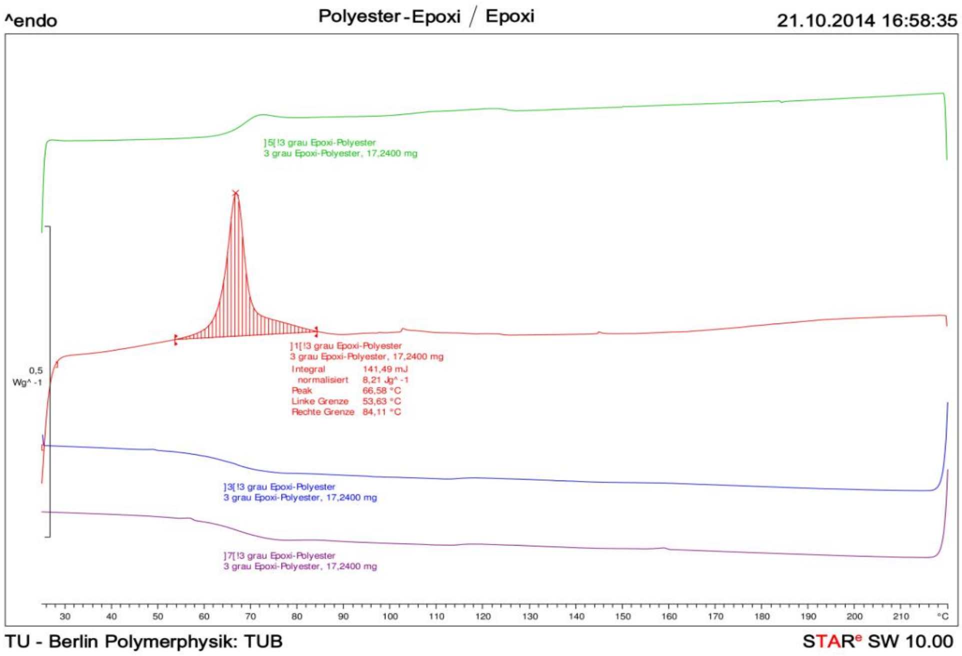

Figure 2: DSC result for thermosetting structured mixed (polyester/epoxy and epoxy) powder coating residue

Figure 2 shows the DSC analysis result for polyester/epoxy and epoxy system mixture powder coating residue graphically. The variance line depicted with red shows the reaction that the sample gave to the temperature increase during the initial heating. Based on this variance, powder coating residue absorbs heat from the medium between 53 and 84^{o}C, creating an endothermic region. The peak point for this endothermic change was identified as 66^{o}C. It could be argued that powder coating commenced to harden over 100^{o}C as a result of temperature increase and an exothermic curve was formed between 100 and 200^{o}C. The green line just over the red line depicts the variance occurred during the second heating.

Since the powder coating was in thermosetting disposition and had hardened in the exothermic region during the initial heating, it did not respond to the second heating and no changes were observed in its structure. The blue and purple lines towards the bottom of the graph show the cooling that was implemented after each heating process. Similarly, since the material was hardened at the end of the first heating, there were no variation during both cooling processes, only glass transition temperatures were observed.

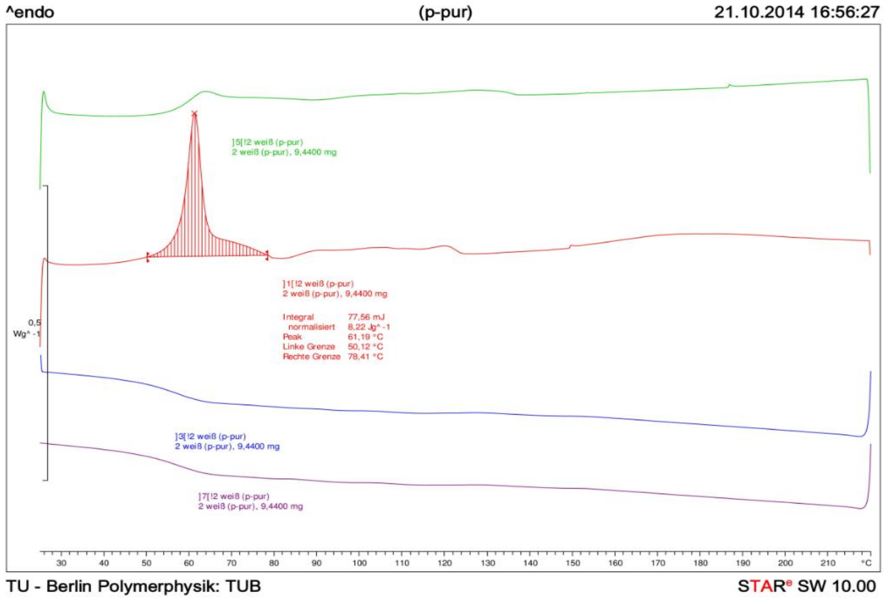

Figure 3: DSC result for thermosetting polyester/polyurethane (p-pur) powder coating residue

The graph that shows the DSC results for thermosetting polyester/polyurethane system electrostatic powder coating residue is presented in Figure 3. It was observed that an endothermic region was formed between 50 and 78^{o}C as a result of the first heating shown with a red line and an endothermic peak point was formed at 61^{o}C.

Furthermore, it could be observed that the material was hardened approximately between 120 and 180^{o}C with absorbing heat from the medium. Since this powder coating was also in thermosetting disposition and due to the hardener in its composition, it was hardened at the end of the first heating and did not react to the second. Second heating and crystallization curves showed that the glass transition temperature for the material was between 55 and 60^{o}C.

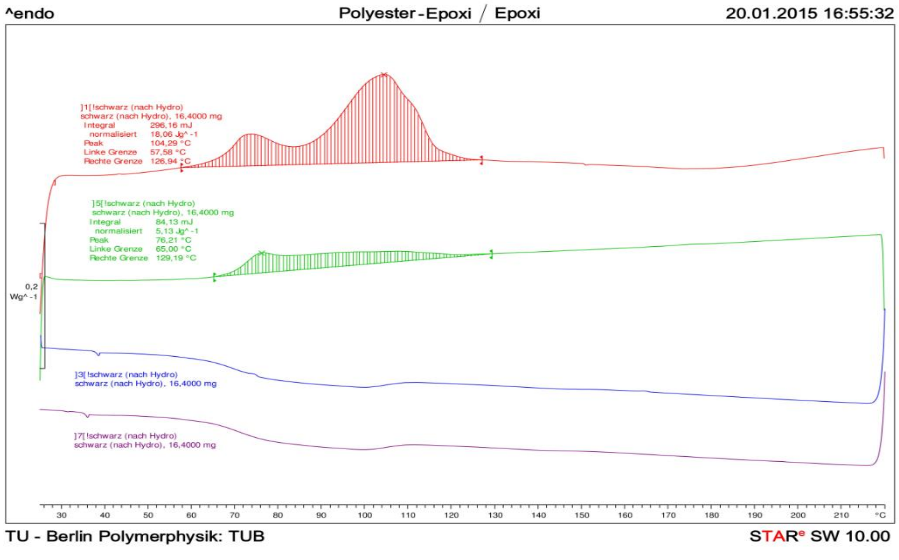

Figure 4: DSC result for hydrolyzed mixed (polyester/epoxy and epoxy) powder coating residue

As a result of the initial heating, depicted with a red line in Figure 4, an endothermic region was formed between 57 and 126^{o}C. It was observed that the temperature range of this region was larger that the one in Figure 2 and peaked at two points. The first peak point was at approximately 70^{o}C and it was a result of the reaction that powder coating gave to the temperature increase. The second peak was due to 1-butanol alcohol, which has a boiling point of approximately 118^{o}C, and used in the hydrolysis of the powder coating. Furthermore, it could be observed that hardening occurred approximately between 140 and 220^{o}C, and the exothermic region was formed along the same line. While non-hydrolyzed powder coating did not react to the second heating, an exothermic region was formed as a result of the second heating depicted by the green line in Figure 4 between 65 and 129^{o}C, and a peak was formed at 76^{o}C. It is possible to state that the structure of the powder coating deteriorated as a result of hydrolysis due to water and alcohol and there was still alcohol in its content with the endotherm region formed at the end of the second heating.

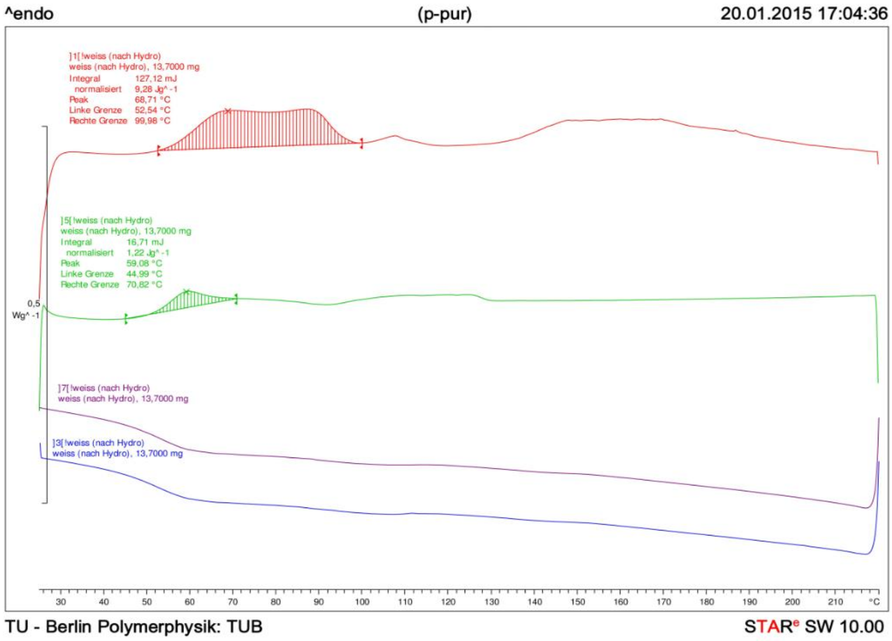

Figure 5: DSC result for hydrolyzed polyester/polyurethane (p-pur) powder coating residue

DSC results for hydrolyzed polyester/polyurethane system powder coating residue are presented in Figure 5. Based on the variance at the end of the initial heating, an endothermic region was observed between 52 and 100oC. Following the endothermic region, an exothermic line was observed where the material released heat to the medium and hardened. Related powder coating also extracted heat from the medium during the second heating due to the effects of hydrolysis and an endothermic region was formed.

3.2 KOFLER HOT BENCH

Hot bench results for two different electrostatic thermosetting powder coating residues given in Table 1 before and after hydrolysis are presented in the figures below.

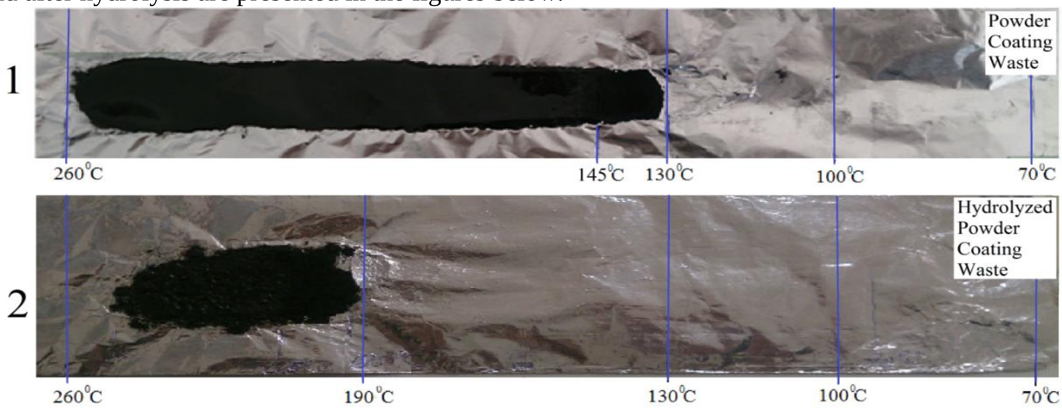

Figure 6: Hot bench results for powder coating residue consisted of polyester/epoxy and epoxy systems (1) before and (2) after hydrolysis.

The figure above depicts hot bench results for mixed black colored electrostatic powder coating residue. The top figure shows results for non-hydrolyzed sample, while the figure below shows the values for the sample obtained via hydrolysis with 20:1 water alcohol mixture. Both samples were cleaned from the aluminum foil using apparatus after heating and cooling processes to determine their properties of adhesion to surface as a result of the heat effect. Non-hydrolyzed powder coating residues shown at the top in Figure 6 were completely cleaned from the surface of aluminum foil between 70 and 130^{o}C, however stuck on the foil surface over 130^{o}C creating a film coating on the surface. However, hydrolyzed samples shown in the bottom of the same figure were cleaned from the aluminum foil surface easily until 190^{o}C. Thus, adhesion temperature was postponed for 60^{o}C.

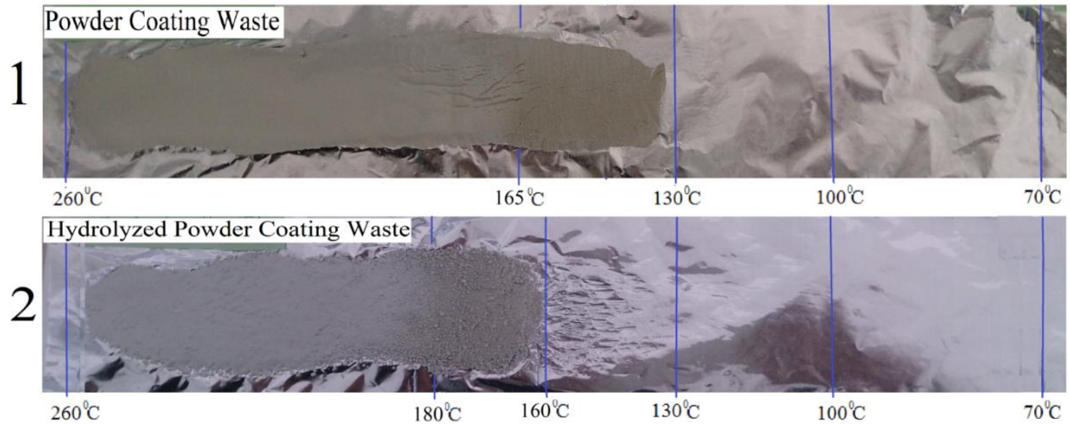

Figure 7: Hot bench results for polyester/polyurethane (p-pur) powder coating residue (1) before and (2) after hydrolysis

Hot bench results for thermosetting polyurethane system powder coating residue are presented in the figure above. Residues were heated for 10 minutes with Kofler hot bench and left for cooling for a few minutes. Non-hydrolyzed powder coating residue shown at the top graph in Figure 7 was cleaned off the surface of the aluminum foil until 130^{o}C. Similarly, the hydrolyzed residue shown at the bottom was cleaned off the surface of the aluminum foil until 160^{o}C. Thus, the temperature that polyester/polyurethane system powder coating residues start to form a film coating by adhering to the metal surfaces was postponed for 30^{o}C. Furthermore, it was observed that a transitional region was formed between 160 and 180^{o}C, and the material preserved its granular structure until approximately 180^{o}C. After that temperature, it was observed that it completely melted and covered the surface.

In other words, residues became workable under higher temperatures without any adhesion to metal surfaces. This was a significant step towards the recycling of residues using different techniques.

IV. CONCLUSION

Study results could be summarized as follows:

(1) It was determined as a result of DSC findings that thermal properties of two electrostatic powder coating system residues were altered via the hydrolysis process. Non-hydrolyzed powder coating residues only reacted to the first heating and demonstrated variance as a result of the second heating. DSC results obtained for the same residue after hydrolysis demonstrated that they reacted to both heating processes due to their alcohol content and the endothermic region created during the first heating covered a wider temperature range. Similarly, the residues extracted heat from the medium during the second heating due to the alcohol content resulting in endothermic regions.

(2) Hot bench results also showed that hydrolysis of powder coating residues changed their structure. Powder coating residues that adhered to metal surfaces at lower temperatures before hydrolysis became workable at higher temperatures after hydrolysis and the adhesion to surface temperatures was deferred for 30 – 60^{o}C.

As per these results, it was demonstrated that polyester/epoxy and epoxy system electrostatic thermosetting powder coating residues could be worked with until 190^{o}C with hydrolysis, and polyurethane residues could be worked with until 160^{o}C in thermal process machines (extruder, plastic injection, hot pressing, etc.) readily.

V. Acknowledgements

This study was supported by Scientific and Technological Research Council of Turkey (TUBITAK) (Project Number: 213M461). The authors are gratefully for this financial support.

REFERENCES

[1] Kısmet, Y., *Entwicklung eines Verfahrens für die Verwertung von Pulverlackrecyclaten*. Berlin: Universitätsverlag der TU Berlin; 2012.

[2] Pietschmann, J., Industrielle Pulverbeschichtung. Wiesbaden: View&Sohn Verlag; 2003.

[3] De Lange, P.G., Powder Coatings-Chemistry and Technology. Hannover: Vincentz Network; 2004.

[4] M. Camargo, M.M.C. Forte, C.R Wolf, Linear density polyethylene thermal fraction by DSC technique, International Journal of Polymer Analysis and Characterization, **18, 2008,** 49-65.

[5] C. Gioian, A. Minesso, C.P. Marchese, A. Celli, M. Colonna, Powder coatings for indoor applications from renewable resources and recycled polymer, Journal Coating Technology Research, 55, 2015, 555-562.

[6] E. Dogan, A.E. Acar, The use of anhydride linkages to increase the glass transition temperatures of polymers containing carboxyl end groups: A perspective in powder coatings, Progress in Organic Caoting, 76, 2013, 513-518.

[7] S. Montserrat, Y. Calventus, J.M. Hutchinson, Physical aging of thermosetting powder coatings, Progress. in Organic Caoting, 55, 2006, 35-42.

[8] F. Wang, R. Martinuzzi, J.J.X. Zhu, Experimental study of particle trajectory in electrostatics powder coating process, Powder Technology, 150, 2005, 20-29.

[9] L. Gherlone, T. Rossini, V. Stula, Powder coatings and differential scanning calorimetry: the perfect fit, Progress in Organic Caoting, 34, 1998, 57-63.

[10] C. Wadenpohl, Production of powder coatings with defined particle size distribution by grinding and inline classification, International Journal of Mineral Processes, 74, 2003, 155-164.

[11] S.S. Lee, J.H. Koo, S.S. Lee, S.G. Chai, J.C. Lim, Gloss reduction in low temperature curable hybrid powder coatings, Progress in Organic Caoting, 46, 2003, 266-272.

[12] K. Pendi, M. Mills, J. Bastien, P. Henshaw, Thermosetting powder coating: Finish apprearance and durability at cure window corner points, Progress in Organic Caoting, 78, 2015, 411-418.

[13] A. Husain, S.A. Bahar, J. Chakkamalayath, A. Vikreman, A. Ghamdi, T. Kamshad, R.S. Siriki, Differential scanning calorimetry and optical photo microscopy examination for the analysis of failure of fusion bonded powder epoxy internal coating, Engineering Failire Analysis, 56, 2015, 375-383.

[14] K.S. Ooi, D.W. Cook, P.G. Simon, H.C. Such, DSC studies of the curing mechanisms and kinetics of DGEBA using in imidazole curing agents, Polymer, 41, 2000, 3639-3649.

[15] G. Gheno, R. Ganzerla, M. Bortoluzzi, R. Paganica, Determination of degradation kinetics of two polyester thermosetting powder coatings using TGA and colorimetric analysis, Progress in Organic Caoting, 78, 2015, 239-243.

[16] R.S. Gamal, M.H. Abdallah, S. Mohamed, A. Abdel, A. Nadia, M. Mohamed, M.W. Sabaa, Cure kinetics and thermal stability of maleimide modified epoxy TGIC/CPE powder coating system. Thermochimica Acta, 617, 2015, 191-199.

[17] P. Castell, M. Wouters, H. Fischer, D.G. With, Kinetic studies of a UV-Curable powder coating using photo-DSC, real time FTIR and rheology. Journal of Coating Technology Research, 4, 2007, 411-423.

[18] X. Ramis, A. Candenato, J.M. Morancho, J.M. Salla, Curing of a thermosetting powder coating by means of DMTA, TMA and DSC. Polymer, 44, 2002, 2067-2079.

[19] R. Mafi, S.M. Mirabedini, M.M. Attar, S. Moradian, Cure characterization of epoxy and polyester clear powder coatings using differential scanning calorimetry (DSC) and dynamic mechanical thermal analysis (DMTA), Progress in Organic Caoting, 54, 2005, 164-169.

[20] Y. Kısmet, Effects of Hydrolyzed electrostatic powder coating wastes on fluidity and density of polyolefins. Sigma Journal Engineering and National Science, 33, 2015, 377-383.

[21] D. Stahlberg, M. Johansson, Properties of powder coatings in load carrying construction. Journal Coating Technology Research, 2, 2006. 473-481.