A STUDY ON WEIGHT LOSS RATE CONTROLLED BINDER REMOVAL FROM PARTS PRODUCED BY FDC

Senol Pekin * [Ψ], John Bukowski [δ], and Avigdor Zangvil *,

* Materials Research Laboratory, University of Illinois at Urbana-Champaign, Urbana, IL.

[Ψ] Energy Technology Division, Argonne National Laboratory, Argonne, IL.

[δ] Center for Cement Composite Materials, University of Illinois at Urbana-Champaign, Urbana, IL.

The binder removal schedule of a binder in the ethylene vinyl acetate-wax system was analyzed by automatically adjusting the soaking duration based on the monitored weight loss of the polymer. The thermolysis of several grades of microcrystalline wax and ethylene vinyl acetate have been analyzed by TGA and DSC to support the explanation of the weight loss rate controlled binder removal experiments. During the thermolysis of such binders in air, the degradation sequence is degradation and evaporation of hydrocarbons, degradation of the vinyl acetate, and degradation of the ethylene chain, all oxygen assisted. It was shown that the extent and the rate of the vinyl acetate degradation in air is determined by the molecular weight of the EVA, unlike its degradation in N_2. It was concluded that thermolysis of light polymers is easier than that of the heavy ones and weight loss rate controlled binder removal technique can help in the optimization of binder removal schedule for a variety of polymers.

I. Introduction

Fused deposition of ceramics (FDC) is a rapid prototyping technique in which a set of 3-D coordinate values can be used to manufacture a ceramic green body. While this method is not suitable for manufacturing an item in large quantities, it is ideal for manufacturing components for which the geometry needs to be tailored on a case by case basis, such as in the cases of biomedical implants and prototype development.

A typical process route in FDC involves milling of the ceramic powder, mixing the organic additives (binder) with the powder, extruding the filament feedstock, solid freeform manufacturing, binder removal and sintering. The binder used needs to have a low melting point (100-150°C), and low viscosity and tackiness upon melting [1]. In addition, since all organic additives are temporary additives in ceramic processing, physical and chemical phenomena that take place during binder removal must be considered for binder formulation. Several types of defects such as carbon retention, cracking, blistering, warping, anisotropic shrinkage and delamination of the sintered bodies can be introduced during the binder removal process [2, 3]. On the other hand, the binder removal process plays an important role in the through-put and the yield of the production [2].

In formulation of a binder system for FDC, four inter-conflicting issues arise:
a) since the FDC requires thermoplastic binders with low viscosity (perhaps the lowest among the paste shaping methods), a binder system with low molecular weight needs to be chosen,

b) in order to minimize the binder content (to decrease volumetric shrinkage after binder removal) or to increase the handling strength of the filament feedstock, a binder system with high molecular weight needs to be considered,

c) a binder with a low viscosity creates difficulties due to the possibility of deformation or slumping during the thermolysis [4], and

d) since the rate of loss of molecular weight (number average) is nearly proportional to the square of the molecular weight, removal of a binder system with a high molecular weight creates difficulty during the thermolysis [5].

Strategies for binder removal include thermal debinding, wicking, solvent extraction and supercritical fluid extraction [2, 3, 6]. Complex chemical processes such as evaporation (endothermic process) of low molecular weight organic additives and degradation (generally exothermic process) of higher molecular additives, and physical processes such as redistribution of the binder throughout the green body take place during the removal process.

Several studies [7, 8, 9] have been conducted to monitor the changes that take place during the binder removal. These changes can include weight loss, heat exchange between the sample and the surroundings, and the dimensional change. Factors affecting the binder removal process include the polymer chemistry and structure, polymer loading, chemical interactions at polymer-ceramic interfaces, heat/mass transport, component geometry, firing atmosphere, and heating cycle [2, 8]. Therefore, optimization of binder removal schedule (i.e. temperature, time, and atmosphere) via analysis of the physico-chemical processes that occur during the thermolysis can be time consuming in rapid prototyping where ceramic powder, the exact binder formulation, and the part geometry need to be tailored within strict time limitations, due to the nature of the process. Therefore, a binder removal process in which the change in one or more of the parameters mentioned above will be automatically kept within the specified limits needs to be incorporated into rapid product development by FDC. The specific limits can be identified by trial-and-error design experiments [see, for example, 9].

In this study, a binder removal system based on monitoring the weight loss of the green component during thermolysis was developed, and incorporated into a research-scale process which aims at the rapid prototype development by FDC. The idea of rate controlled decomposition was suggested by Rouquerol [10] to study the apparent orders of reaction, energies of activation and differential enthalpies of dissociation, especially under high vacuum, and attempts have been made to employ such a technique in binder removal from ceramic green bodies. For example, a rate controlled extraction system [8] has been constructed which adjusts the (soaking) temperature of the furnace based on the weight-loss of the organic constituents. Following an evaluation of binder removal strategies and rate controlled binder removal systems, a rather complex procedure based on the PI (proportional-integral) control of the weight signal by means of the furnace temperature in an adaptive cascade configuration has been proposed [7]. However, the present study is different from the previous attempts, since a) it aims the determination of the soaking duration at each temperature reached, b) it is easy to incorporate into any vertical-tube furnace by the help of a data acquisition system capable of generating digital output signal, and c) it is used together with analysis of physico-chemical events that

occur during the pyrolysis in order to develop binder removal schedules in rapid ceramic prototype development.

II. Experimental Procedure

A binder removal system based on monitoring the weight loss of the green component during thermolysis was constructed as described in Figure 1. The microcomputer commands the data acquisition system via a standard LPT port. The weight of the sample is monitored by a Mettler PJ300 digital balance equipped with a dedicated RS-232 board. The heart of the set up is a software (named DB3) developed specifically for this purpose and written in Labview. The software reads and averages the weight via the balance and converts this information into actual weight loss rate, $(WLR)_{actual}$, in each time interval, the duration of which is defined by the user. In this study, a two-minute long time interval was used. If the absolute value of $(WLR)_{actual}$ is larger than a user defined value, the software sends a signal to a relay board which switches the furnace controller into "hold"; and therefore, initiates a soaking duration at that temperature. Once initiated, the number of intervals (hold period) that a hold command remains valid can also be entered by the user. During the hold period, if another $(WLR)_{actual}$ value that falls outside the user defined limit is detected, the count-down of the hold period is re-started. If all of the $(WLR)_{actual}$ values detected during a hold period remain within the user defined limits, the hold period lasts the number of intervals that was defined by the user.
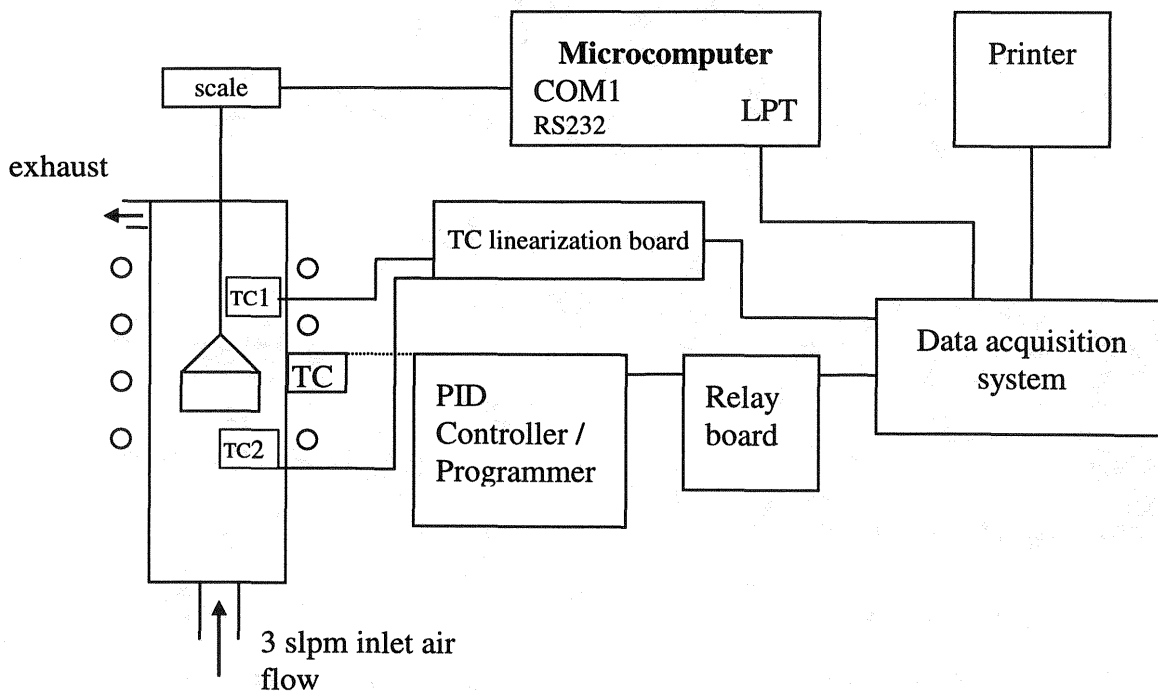

Figure 1. The schematic of the weight loss rate controlled binder removal system.

The sample was placed in a basket made of Inconel 601 alloy and was lowered into the hot zone of the furnace via the hook of the balance. In such a system oscillations cause sinusoidal

fluctuations in the balance readings. To overcome this effect a user defined value was introduced as the derivation interval as shown in figure 2.

A derivation interval of 7 was used in this study. The furnace was controlled by a PID controller which read the temperature of the furnace tube. The controller was programmed to heat the furnace at a rate of 15°C/hour up to 600°C. An upward air flow rate of 3 slpm was used. The direction of heat flow between the sample and the furnace atmosphere was monitored roughly by placing a thermocouple right below and another one right above the basket which contained the sample.

The samples used in this study contained 40 (wt.) % binder and 60% alumina. The binder itself contained 60% microcrystalline wax (blend of two different grades), 20% of an EVA grade that contains 20 % vinyl acetate, and 20 % of an EVA grade that contains 28 % vinyl acetate. The melt index of the former grade was 8 dg/min, whereas the melt index of the latter was varied between 2500-0.15 dg/min to study its effect in binder removal.
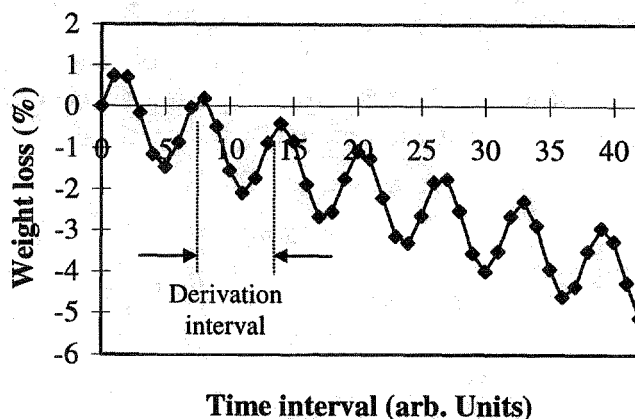

Figure 2: Explanation of the derivation interval. When sinusoidal oscillations are present, a normal derivation (derivation interval =1) would cause incorrect calculation of the weight loss rate.

Thermal analysis was done by using a Netzsch Model STA 409 simultaneous thermal analyzer, at a heating rate of 10°C/hour under flowing air. The solid freeform was fabricated by using a Stratasys FDM 3-D Modeler.

III. Results and Discussions

Prior to the analysis of the data obtained from the rate controlled binder removal system, an understanding of the oxidative degradation of the organic components is needed. The TGA-DSC curves of the wax grades used are given in figure 3 and 4. A microcrystalline wax can be defined as a solid hydrocarbon mixture, of average molecular weight range of 490 to 800 (i.e. appx. 17 - 44 carbons), considerably higher than that of paraffin wax (350 to 420) [11]. Hydrocarbons are formed by the decarboxylation of esters, the removal of the CO_2 resulting in a hydrocarbon with an odd number of carbons. Hydrocarbons found in waxes are mostly saturated open chain series

(alkanes), and to a lesser extent, unsaturated olefins (alkenes) [11]. These hydrocarbons have so low molecular weights that they can readily be evaporated without any chain scissioning. An analogy can be set here with the degradation of polyethylene, $(CH_2)_n$, which is nothing but a very large hydrocarbon chain. Iida et al. [12] reported that degradation of PE under N_2 atmosphere provides products up to ~C_{20}. Furthermore, it was reported [13] that molecules as large as $C_{94}H_{190}$ can evaporate without decomposition in vacuum. Those molecules that are too large to evaporate decrease their chain length by undergoing an oxidative degradation process prior to evaporation. Jellinek [14] studied the mechanism of degradation of straight and branched type ethylene chains in vacuum, and proposed a mechanism in which the first or last monomer unit is broken off the chain. Dickens [15] studied the process in more detail and suggested that the end radicals extract hydrogen from the surrounding polymer matrix to form backbone radicals, and these backbone radicals undergo either β scission or disproportionation. Activation energy for the decomposition of polyethylene increases as the molecular weight of the polymer increases, and was reported to be in the range of 50-70 kcal/mole in vacuum [14, 15], and 20 kcal/mole for oxidation [15]. This argument is in good agreement with the results shown in figure 3 and 4. The microcrystalline wax given in figure 3 has more light hydrocarbons than the one given in figure 4, as the melting endotherms given in the insets indicate. Thus, the light hydrocarbons in the former wax can evaporate without much degradation which is proven by the large endothermic peak in the DSC curve.
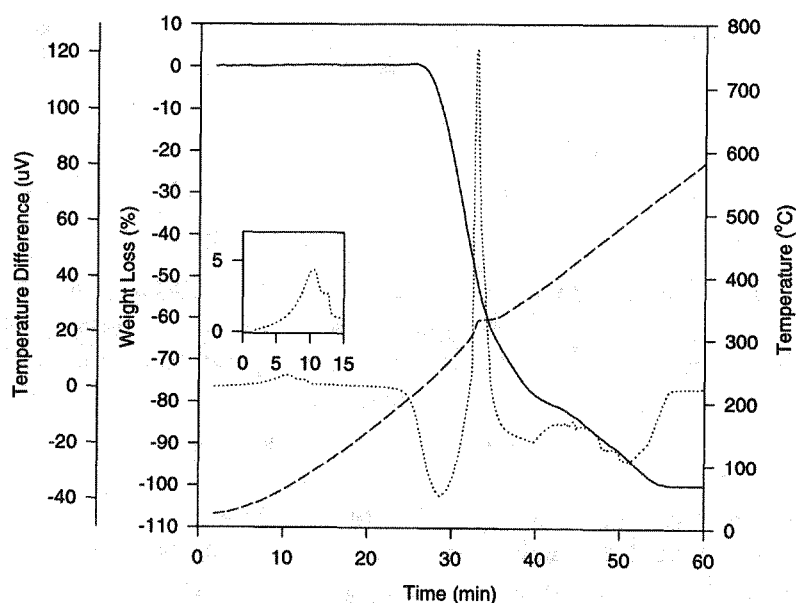

Figure 3: The TG (——)and DSC(·······) curves for the thermolysis of lower melting point grade microcrystalline wax. The first exotherm indicates the onset of the chain scissioning of the heavier hydrocarbons; whereas the following endotherms indicates the evaporation of the light components. The inset is a close-up of the melting endotherm of the DSC curve.

From a binder removal point of view, highly endothermic removal of a component can create a high temperature gradient between the furnace atmosphere and the remaining components of the binder system. It can be speculated that during the evaporation of the hydrocarbons in the microcrystalline wax, the next exothermic process would be surpressed. Once this endothermic

process is completed, the temperature of the sample would increase suddenly and the onset of the exothermic process would shift to higher temperatures. As far as the weight loss curves are concerned, it is obvious that the removal of microcrystalline wax is gradual and takes place between 250 and 450°C . This removal opens up free space in the green body, thus higher removal rates of the remaining organic components can be tolerated. A careful analysis of the TG curves reveals a weight gain at about 150°C right before the weight loss starts. This weight gain can be attributed to the oxygen uptake [16], and since this weight increase is more profound in the wax grade that contains heavy hydrocarbons, it verifies that oxygen assists in the chain scissioning process.
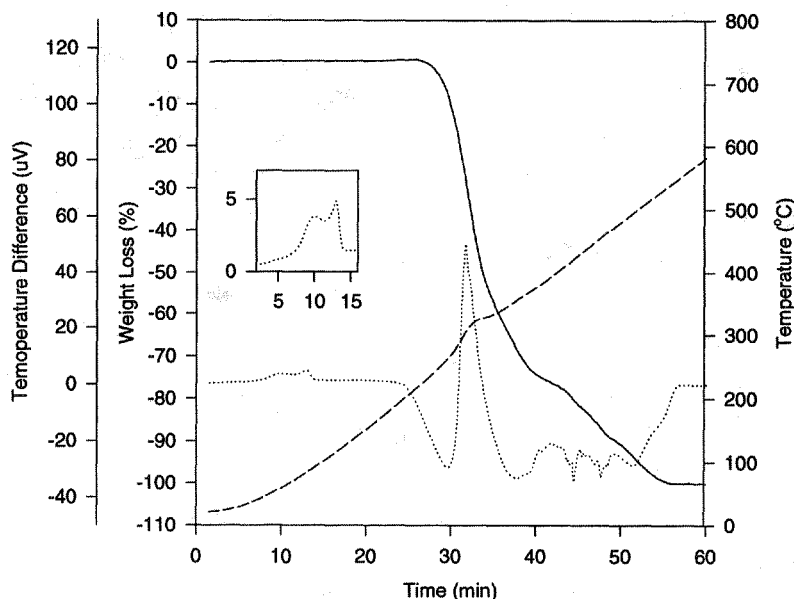

Figure 4: The TG (—)and DSC(·····) curves for the thermolysis of higher melting point grade microcrystalline wax. As shown in the inset, this wax has a significant amount of heavy hydrocarbons. The heat needed for evaporation is supplied by the exothermic oxidation reaction progressing in parallel. As a result, the range of the temperature difference, which is proportional to the change in heat flux, is smaller than the one in figure 3.

A typical TGA-DSC curve for degradation of EVA in flowing air is given in figure 5, for a 28% vinyl acetate containing grade. It has been shown [17, 18] that degradation of EVA in nitrogen atmosphere takes place in two steps: one for the degradation of the vinyl acetate chain and one for the degradation of the ethylene chain, as also shown in figure 5. The reported onset of the first step corresponds to 350°C whereas the maxima of the Gram-Schmidt intensity peak for the same step corresponds to 364°C [17]. It was also reported that the heating rate has no effect on the onset, rate or extent of this decomposition [18]. In this study, however, degradation studies carried out in air showed that molecular weight of the polymer has a significant effect on a)the extent and the rate of the pyrolysis of the vinyl acetate chain, and b)the rate of pyrolysis of the ethylene chain. The first step is slightly exothermic in general, whereas the second step displays first an exothermic and then an endothermic peak. The range of the temperature difference between the two opposite peaks was especially high for the high molecular weight grades. The

fact that the rate of the pyrolysis of the ethylene chain increases as the molecular weight increases can be explained by what Casassa had proposed [5]: If the degradation is a first-order reaction, the rate of destruction of the polymer links at some temperature is:

$$-\frac{dp}{dt} = kp$$

where p is the number of monomeric units held together by polymer linkages. Integration of this equation gives:

$$-\int_{p_\infty}^{p} \frac{dp}{p} = k\int_{0}^{t} dt \text{, or } \ln\left(\frac{p_\infty}{p}\right) = kt,$$

where p_∞ is the number of polymer links in a given volume of a system consisting of polymer of (infinitely) high molecular weight. Since $p = p_\infty\left(\frac{n-1}{n}\right)$, where n is the number of monomer units per molecule [5];

$$-\left(\frac{dn}{dt}\right) = k(n^2 - n) \text{, or as a good approximation at high molecular weight; } -\left(\frac{dn}{dt}\right) = kn^2$$
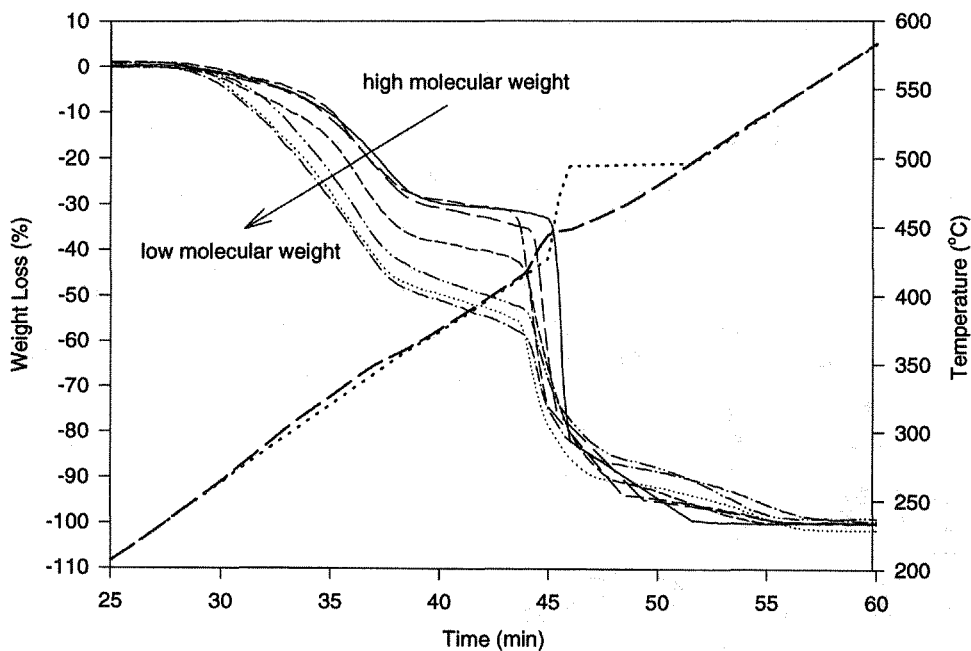

Figure 5: The TGA curves for the thermolysis of EVA (28% VA) with weight average molecular weight in the range from 29990 to 119900. The first weight loss step is due to oxy-degradation of the vinyl acetate and the second step is due to the oxy-degradation of polyethylene chain. The (·······) and (----) are the temperature vs. time curves for the highest and the lowest molecular weight polymers, respectively.

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Thus, during a degradation reaction of the first order with respect to reacting groups, the rate of loss of molecular weight (number average) is nearly proportional to the square of the molecular weight. In the case of oxidative degradation, the rate of destruction of the polymer links may not be necessarily first order; however, Casassa also argued that the result would still be the same at high degree of polymerization without such an assumption.

The result of a pyrolysis experiment of a part produced by FDC [19] is given in figure 6. The molecular weight of the EVA (28% vinyl acetate) was 99360 [19]. In figure 6, it is clear that there is overall weight gain up to 200°C furnace temperature (TC). The feedback for the control of the furnace temperature is provided by a thermocouple that senses the temperature of the furnace chamber to avoid the interference from the pyrolysis heat. The weight gain is followed by evaporation of scissoned or light hydrocarbons. Pyrolysis of rather heavy chains (ethylene chain of the EVA) takes place right above 400°C (TC) and at a narrow temperature range. As seen in figure 6, the DB3 algorithm was not able to control the weight loss rate during the EVA pyrolysis as strictly as it did during the pyrolysis of the wax, when the user defined value of the hold period was 4 intervals. However, the control of such rapid pyrolysis reactions can be improved by increasing the hold period via the DB3 software. The fluctuations in the TC2 thermocouple reading that started above 200°C (TC), were attributed to spattering of the polyethylene.
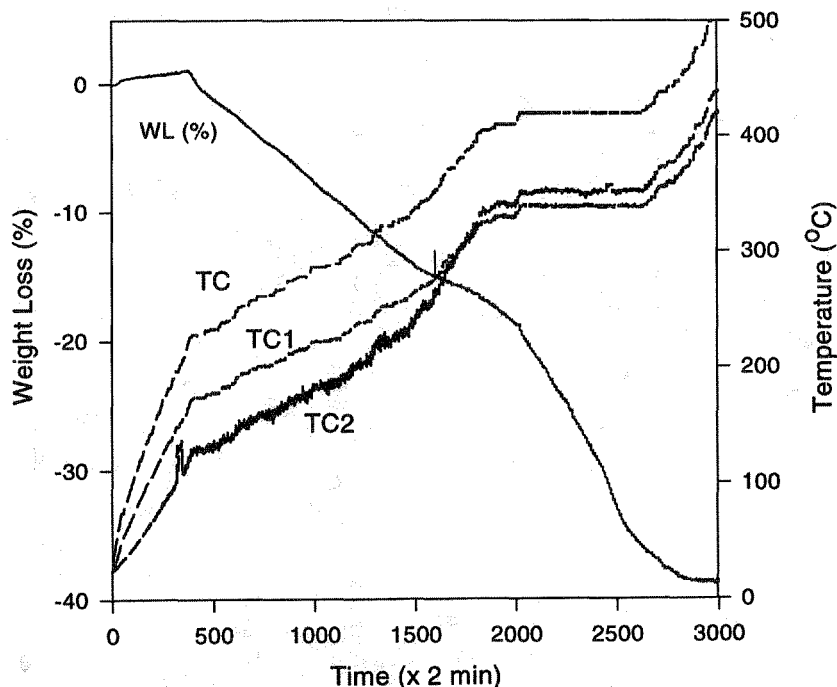

Figure 6: The controlled pyrolysis weight loss and the resulting temperature curves of a green body produced by FDC, and containing a binder in the EVA-wax system. The soaking duration at each temperature was controlled by specifically developed DB3 algorithm which allowed the temperature increase at 15°C/hour only if the measured weight loss rate was within the +/- 0.015 % per two-minute long interval (see figure 1 for details).

IV. Conclusions

Thermal analysis of the organic components used in the binder system based on EVA-wax blends revealed that the degradation sequence is degradation and evaporation of hydrocarbons, degradation of the vinyl acetate, and degradation of the ethylene chain, respectively. It was shown that degradation of EVA in air is different than its degradation in N_2. The extent and the rate of the vinyl acetate degradation in air is determined by the molecular weight of the EVA. It was also shown that degradation rate of the ethylene chain in EVA increases as its molecular weight increases. These thermal analyses were carried out to support the explanation of the weight loss rate controlled binder removal experiments.

A system that determines the soak duration at each temperature during heating up for binder removal has been set up. It was shown that, under given control parameters, removal of the wax can be done precisely, whereas controlled removal of the heavier components is rather difficult, and an example was given for the binder that contained EVA with a molecular weight of 99360.

A rate-controlled binder removal system can control chemical events taking place during the binder removal. Since low viscosity binders are used in FDC, physical events take place during binder removal from parts produced by FDC can be very important. Therefore, optimization of rate-controlled binder removal schedule, especially for parts produced by FDC, needs to be supported by an understanding of the physical phenomena as well.

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