Binder Formulation in EVA-wax system for Fused Deposition of Ceramics

Senol Pekin * Ψ, Avigdor Zangvil *, and William Ellingson Ψ
* Materials Research Laboratory, University of Illinois at Urbana-Champaign, Urbana, IL.
Ψ Energy Technology Division, Argonne National Laboratory, Argonne, IL.

Blends in the ethylene vinyl acetate (EVA) – wax system have been evaluated as potential binders to be used in fused deposition of ceramics (FDC). In order to obtain good handling strength, it was indicated that the melting point of the polymer needs to be lower than that of the wax. In this context, it was shown that the melting point of the EVA decreases as the vinyl acetate content in the copolymer increases. By measuring the viscosity as a macroscopic property, it was shown that 20 % vinyl acetate-containing EVA is miscible in microcrystalline wax up to, at least, 30 %. Binders used in FDC need to have low viscosity and it was pointed out that the slumping can be one main problem associated with binders with low viscosity. Thus, thermolysis of wax at low temperature is suggested as a solution. The volumetric thermal expansion and melt strength of an EVA-wax blend were displayed as a function of temperature, in the form of a penetration test.

I. Introduction

Fused deposition of ceramics (FDC) has recently emerged as a new way of shaping ceramic components [1]. The method has advantages in the sense that it minimizes the product development time and cost; however, it also imposes several challenges regarding the ceramic processing. The main challenge lies in the binder development and in the optimization of the properties of the feed-stock material. Binder development has traditionally been a complex issue since it is related not only to the binder formulation but to optimization of the removal conditions as well. Therefore, mechanistic understanding of the physico-chemical processes that occur during thermolysis and information related to the rheology of the binder system are needed. In addition, the FDC method imposes several requirements for the binder system.

In this study, the requirements of a binder system to be used in FDC are classified into two categories: general and secondary. The general requirements are low melting point, low viscosity and tackiness. The secondary requirements are those that gain importance during specific processing stages (e.g.; extrusion, debinding, etc.) and are wetting ability (γ_{SL} and γ_{SV}), melt strength, melt index, shear-thinning behavior, handling strength, (steric) stabilization ability, residue content, etc.

A typical processing sequence for FDC involves milling of the ceramic powder, mixing the organic additives with the powder, extrusion of the feed-stock filament, solid freeform fabrication, binder removal and sintering. For example, shear-thinning behavior and appropriate melt strength are required during the extrusion of the small-diameter (< 2 mm) filament. The FDC is the only ceramic shaping method that requires no die or mold, and, hence, the liquid-air interfacial energy of the binder system determines the surface finish of the sintered body. The requirement for the level of the paste viscosity upon melting is perhaps the lowest one among the ceramic shaping techniques. For example, in injection molding and extrusion, the acceptable viscosity is higher than that for the FDC, since the former methods employ force for shaping the component. However, low viscosity of the binder above the melting point can cause deformation ("slumping") during the binder removal stage [2]. Below the melting point, strength of the binder is important for handling the filament.

These requirements limit the binder formulation to a thermoplastic one. Thermoplastic polymers can be semicrystalline (e.g.; polyethylene, polypropylene, nylon) or glassy (e.g.; polystyrene, polyvinyl chloride). A semicrystalline polymer becomes viscous liquid when melted, whereas a glassy polymer becomes a leathery or viscous dough-like material when heated above its glass temperature, T_g [3,4]. Thus, semicrystalline thermoplastic polymers are suitable as organic additives in FDC.

Since low viscosity is desired upon melting, wax has been the major component of the binder system. Wax is a general name for a variety of compounds that include paraffinic waxes, microcrystalline waxes, synthetic hydrocarbon waxes and oxidized polyethylene waxes [5]. Paraffinic and microcrystalline waxes are by-products of the petroleum industry, whereas synthetic hydrocarbon waxes and oxidized polyethylene waxes are produced by polymerization or oxidation of ethylene, respectively [5]. By adjusting the parameters during the polymerization of ethylene, not only the chain length (as represented by average molecular weight and molecular weight distribution), but also the degree of branching in the polymer (which determines the crystallinity and density) can be adjusted. The very low molecular weight (as low as 400) polyethylene (PE) is used as synthetic wax, whereas the very high end of the range (as high as 5 million) is known as ultra high M_w PE. The degree of branching, on the other hand, determines the crystallinity, and thus, the density of the polymer. The low density polyethylene (LDPE) is highly branched and has about 50 % crystallinity. The high density form (HDPE) has few side-chain branches and has about 90 % crystallinity [6, 7].

Olefins (propylene, 1-butene, 1-hexene, 1-octene) are copolymerized to improve selected properties of HDPE as the density is reduced. Low density copolymers containing varying amounts of vinyl acetate (EVA), maleic anhydride (EMA), ethyl acrylate (EEA) are produced to modify selected physical properties of LDPE homopolymers [6,7].

Properties of wax can be improved by the addition of PE homopolymer or copolymers containing PE. This blending process not only improves the properties of the wax, but also yields a graded volatility binder system. Despite the fact that every polymer has some solubility in every other polymer, the magnitude in most cases is extremely low [8, 9]. Compatibility of the wax with EVA depends on the melting points of the two, and on the vinyl acetate content of the copolymer.

In ceramic processing, organic additives not only aid in the shaping of the component, but also have significant influence on the microstructure, and thus, the properties of the ceramic component. The purpose of this study is to apply general ceramic processing science to FDC, by evaluating different grades of EVA-petroleum wax mixtures as a potential binder. The fact that EVA and the petroleum wax are commercially available in several different grades, make them good candidates to be used as binder components for FDC; therefore, a discussion on the effect of their properties is given in this study.

II. Experimental Procedure

Viscosity of the EVA-wax mixtures was measured by using a Brookfield viscometer with spindle #2. Since thermal gradients develop during non-isothermal viscosity measurement in viscous fluids, a sample holder which is slightly larger than the Brookfield LV2 spindle in diameter, was used. A cooling/heating rate of 30°C/hour was used, while the rotational speed of the spindle was selected depending on the viscosity range of the blend. Penetration tests were performed on the 1 g samples of the blends by using a 0.8 g/mm^2 contact pressure at a heating rate of 15°C/hour in a specially made penetration test apparatus. Melting endotherms of different grades of the EVA, wax, and their blends were characterized by using a Perkin-Elmer DSC-4 differential scanning calorimeter at 10°C/min heating rate, with 5 mg samples, and under flowing N_2. The temperature scale was calibrated by using the melting endotherm of indium sample. Microstructural analysis of the extruded filaments were done by using a Hitachi S-800 SEM equipped with a thermoionic filament, at 10kV accelerating voltage.

The EVA used was supplied by DuPont and was a copolymer of vinyl acetate and polyethylene, whereas the microcrystalline wax used was supplied by IGI. The selected properties of the materials used as claimed by the supplier are given in table 1. The ceramic powder used was Alcoa A-17 grade alumina. The ceramic green bodies were fabricated by using a Stratasys FDM 3-D Modeler.

Table 1: Selected properties of the ethylene-vinyl acetate copolymer grades used, as claimed by the supplier.

V.A. wt. %	M.I. (dg/min)	Avg. M_w	Tensile Strength (MPA)
20	500	49100	4.7
20	8		18
20	2.5	132000	23
25	400	51400	3.3
28	2500	29990	1.6
28	800	40840	2.6
28	400	44010	2.8
28	150		5.5
28	43	99360	9.7
28	25	112000	11
28	6	81900	24
28	3	119900	29
28	0.5		22
28	0.15		23

III. Results and Discussions

In formulation of a binder system for FDC by using wax and EVA, the main factor that determines the handling strength of the filament feedstock are the melting points of the two components. To obtain good strength, the melting point of the weaker component (wax) needs to be higher than that of the stronger one (EVA). During cooling, the wax solidifies first and forms micro globes in the EVA melt, and eventually the polymer solidifies and forms a 3-dimensional network. During the early experiments in this study, it was observed that paraffinic wax-EVA blends don't display handling strength due to the low melting point of the paraffin wax. On the other hand, the melting point of the EVA can be adjusted by the vinyl acetate content, as shown in figure 1. The vinyl acetate disrupts crystallinity of the ethylene chain and decreases the melting temperature of the polymer. At a given vinyl acetate content, the rheological properties of EVA can be adjusted by changing the molecular weight of the polymer. As shown in figure 2, the change in the molecular weight of EVA influences the enthalpy of melting, but not the onset temperature of melting.

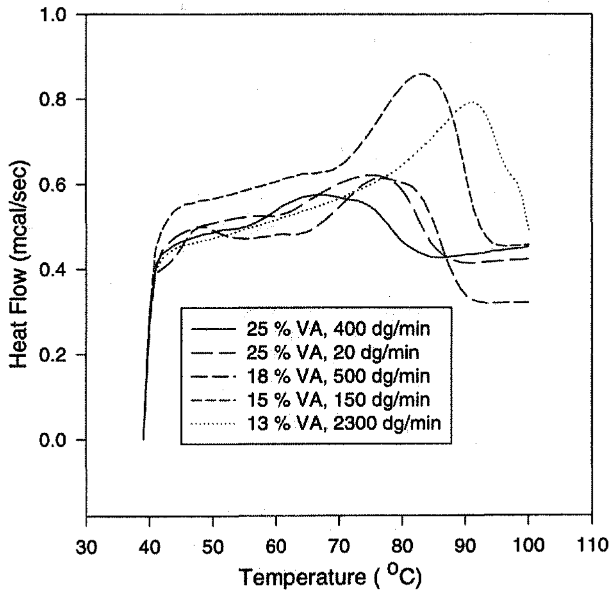


Figure 1: The effect of vinyl acetate content and the molecular weight (as represented by the melt index) on the melting endotherm of the EVA.

The compatibility of the wax-EVA mixtures were monitored by viscosity measurement during both cooling and heating. As shown in figure 3, the EVA containing 20 % vinyl acetate showed compatibility as the weight of the EVA was varied from 5 to 30 %. The fact that the slopes of the curves in the 5-20 % range are almost identical, reveal that the EVA can form a three dimensional network in the solvent wax and can dominate the viscoelastic/viscous flow. The increase in the activation energy at 30 % can be due to the entropic contribution.

Resistance to viscous flow is especially important during the binder removal step, since binders with too low viscosity can cause slumping of the green body. During the thermolysis, since the wax is removed at an earlier stage, the EVA content in the remaining of the binder will increase, and viscosity decrease of the binder system due to temperature increase will be compensated to some extent. Figure 4 shows that the lower temperatures the wax is removed, the higher the

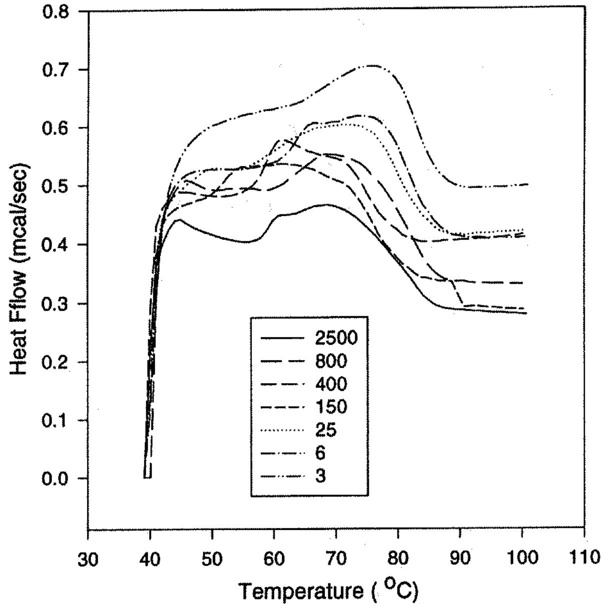


Figure 2: The effect of molecular weight(as represented by the melt index) on the melting endotherm of EVA, containing 28 % vinyl acetate.

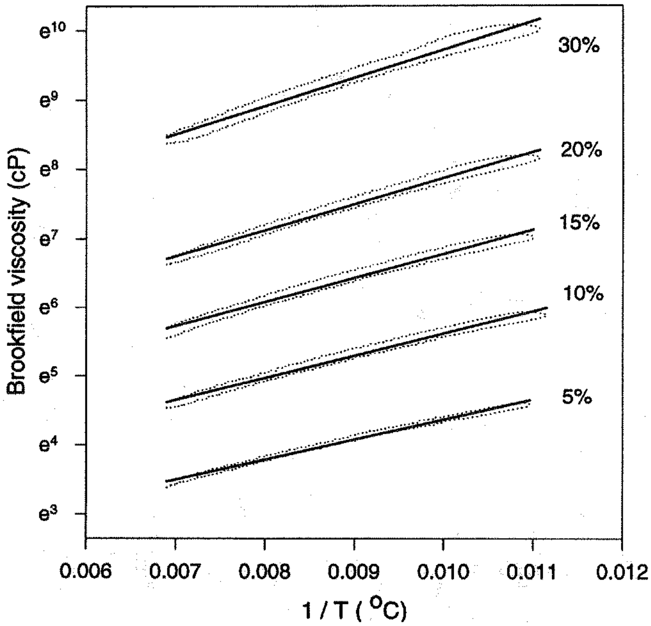


Figure 3: The Arrhenius plot of the viscosity change of the microcrystalline wax - 20 % vinyl acetate containing EVA blends during heating and cooling at a rate of 1.5°C/min. The increase in the hysterisis is due to the increase in viscosity, which in turn causes high thermal gradients in the sample cup during heating or cooling.

increase in the viscosity of the binder system. The viscosity of the binder system, together with the pore size distribution, will also affect the redistribution of the binder within the green body during the binder removal. It was stated that binder will be removed from larger pores first and it will be redistributed towards the smaller pores due to their high suction potential [2].

The dimensional change of the binder is also an important issue, since it can cause stress build up or warping in the green body. The thermal expansion of microscrystalline wax -EVA (20 % vinyl acetate) blends, which continues till the onset of the melting, is shown in figure 5 in the form of a penetration test. In figure 5, the fact that the penetration becomes more gradual as the EVA content increases reveal that melt strength increases as the EVA content is increased. This is to be expected, and a gradual decrease in the melt strength is desirable during the extrusion of the filament feedstock.

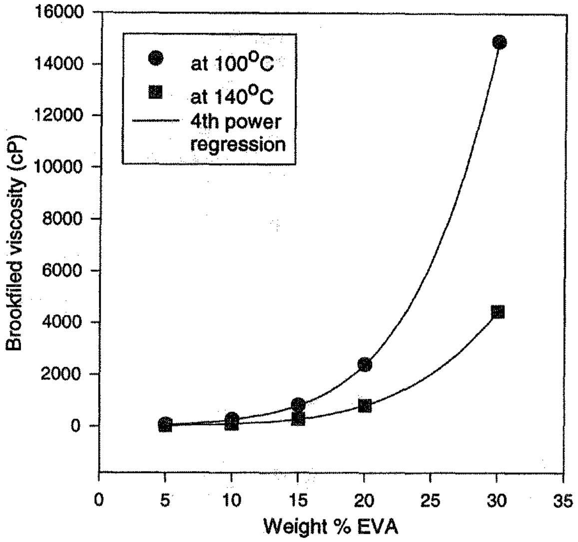


Figure 4: The effect of the EVA content on the viscosity of microcrystalline wax - 20 % vinyl acetate containing EVA blend.

A microstructural evaluation on the fracture surfaces of the filament feedstocks containing 60 % alumina support the previous arguments. The samples contained 24 % microcrystalline wax and 16 % EVA which had 24 % vinyl acetate on average. As shown in figure 6A, the binder that contains the higher molecular weight EVA forms a bulkier network, thus providing better handling strength as compared to the binder with lower molecular weight EVA.
Since all organic additives used in ceramic processing are temporary additives, their removal characteristics from the green body is as important as their functional properties. The pyrolysis characteristics of the binder systems in EVA- wax system developed for FDC is discussed in else where [10].

IV. Conclusions

Binder formulation is a complex issue and several factors need to be considered for intelligent formulation. Blends in the wax-EVA system have been evaluated as potential binders to be used in fused deposition of ceramics. The fact that EVA and wax are available in several different grades make this system an excellent candidate as a potential binder for FDC, and the effect of some of the parameters have been discussed in this study. In order to obtain good handling

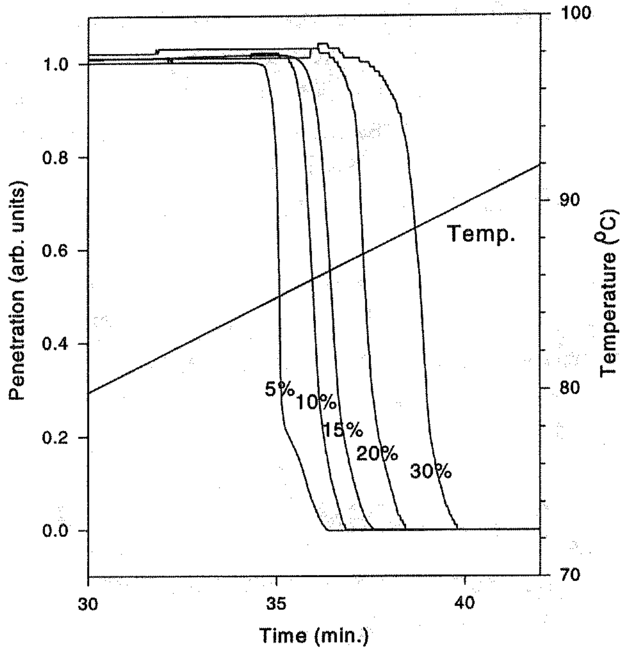
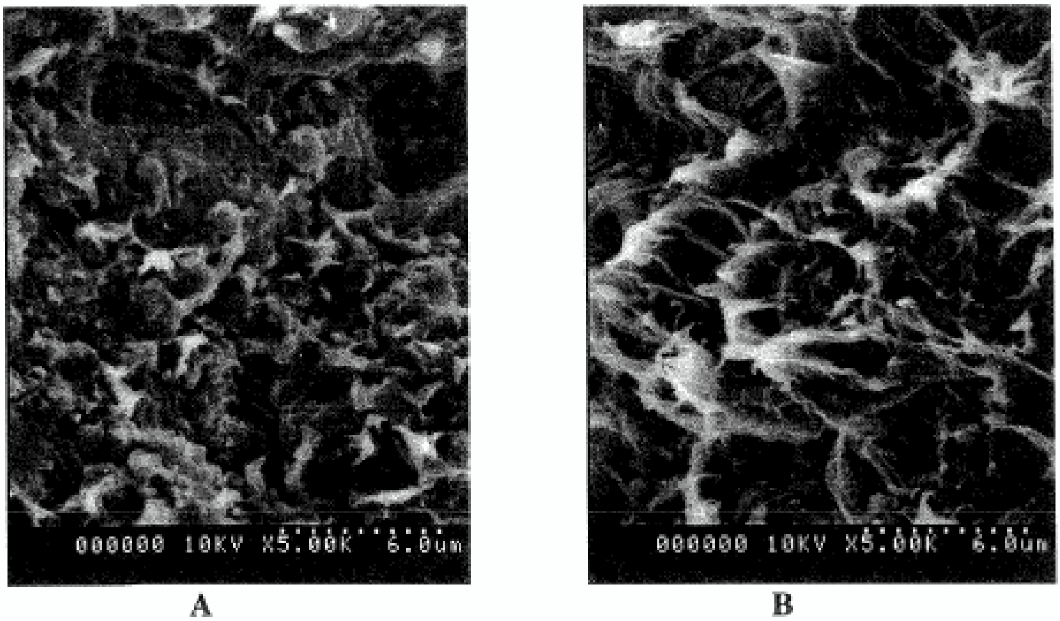


Figure 5: The effect of EVA content on the penetration test result of a microcrystalline wax – 20 % vinyl acetate containing EVA



A

B

Figure 6: Fracture surfaces of (A) alumina green body that contains low molecular weight EVA, (B) alumina green body that contains high molecular weight EVA.

strength, the melting point of the polymer needs to be lower than that of the wax. In this context, it was shown that as the vinyl acetate content in the EVA increases, the melting point of the polymer decreases. By measuring the viscosity as a macroscopic property, it was shown that 20 % vinyl acetate containing EVA is miscible in microcrystalline wax up to, at least, 30 %. Binders used in FDC needs to have low viscosity but their use may cause slumping during binder removal. Thus, thermolysis of wax at low temperature is suggested as a solution. The fact that volumetric change upon heating increases as the EVA content in the binder increases was displayed in the form of a penetration test, which also shows the increase in the melt strength (or softening point) as the EVA content in the binder increases.

Finally, the formulation of a binder system depends not only on the room temperature characteristics, but also on the degradation behavior of the binder. A study on the thermolysis characteristics of the binders in the EVA-wax systems is given in elsewhere [10].

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References:

1) M. K. Agarwala et al., "Structural Ceramics by Fused Deposition of Ceramics", Proceedings of the Solid Freeform Fabrication Symposium, 1995, vol. 6, pp. 1-8, ed. by H. L. Marcus, J. J. Beaman, J. W. Barlow, D. L. Bourell, and R. H. Crawford, The University of Texas at Austin, Texas.
2) M. J. Cima, J. A. Lewis, and A. D. Devoe, Binder Distribution in Ceramic Greenware During Thermolysis", J. Am. Ceram. Soc., 1989, 72 [7] 1192-99.
3) Ceramic Injection Molding, by B. C. Mutsuddy, and R. G. Ford, 1st Ed., Chapman & Hall, Cambridge, UK, 1995.
4) Polymers and Their Properties: vol.1 Fundamentals of Structure and Mechanics, by J. W. S. Hearle, Ellis Horwood Ltd., England, 1982
5) The Chemistry and Technology of Waxes, by A. H. Warth, 2nd Ed., Reinhold Publishing Corporation, New York USA, 1956.
6) Ethylene: Keystone to the Petrochemical Industry, by L. Kniel, O. Winter, and K. Stork, 2nd Ed., Marcel Dekker, Inc., USA, 1980.
7) High Polymers: vol. XI. Polyethylene, by R. A. V. Raff, and J. B. Allison, Interscience Publishers, , New York, USA, 1956
8) Lecture Notes, Polymer Blends Workshop, by D. J. Lohse et. al., Division of Polymeric Materials: Science and Engineering, ACS Spring Meeting, 1998, Dallas, USA.

9) Polymer-Polymer Miscibility, by O. Olabisi, L. M. Robeson, and M. T. Shaw, Academic Press, New York, USA, 1979.
10) S. Pekin, A. Zangvil, and W. Ellingson, "A Study on Weight Loss Rate Controlled Binder Removal from Parts Produced by FDC", Proceedings of the Solid Freeform Fabrication Symposium, 1998, to be published, The University of Texas at Austin, Texas.