Hot Melt Inks for 3D Printing

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Abstract

A unique modified formula of hot-melt ink for phase change printing process was developed. A composition useful for 3D printing comprises different waxes, tackifier and plasticizer resins, rheology modifiers, and UV curable resin and/or gas releasing agent. Differential scanning calorimetry was used to evaluate thermal properties of the ink components and the extensive study of the thermal behavior of the proposed gas releasing agents has been carried out. The rheology behavior of inks and printability such as image detail, definition of dots (sharpness of the edges), dot formation, and spreading were investigated. Dot heights were measured by a modified method using a First Ten Angstrom dynamic contact angle instrument. Sutherland Rub resistance test was also used together with tape adhesion tests for ink adhesion monitoring.

Introduction

The ability to form a raised three-dimensional image makes possible the use of modified processes, inks and substrates in fine art work, such as children's books, business cards, postcards, and special type printing processes. If the raised image attains required height and firmness, it can be used in printing of Braille characters. Production of three-dimensional (3D) images on a substrate can be accomplished by old fashioned embossing procedures, hectographic or spirit duplicating masters, raised Xerographic printing with thermally intumesced electroscopic powders, three-dimensional imaging paper, thermographic process, a special printing process that works by building parts of light curable photo-polymer in layers, or a heat transfer printing with thermally-expandable ink layer.

3D Ink Writing Systems

Three dimensional writing techniques can be divided into two categories:

- Droplet based inks
- Continuous inks

The main idea of ink writing techniques lays in the deposition of colloidal, nanoparticle, or organic based inks to create structures. Because of the containing self-supporting characteristic 3D periodic structures pose the great challenge for designing of those inks. Inks are typically formulated from colloidal, polymeric, or polyelectrolyte suspended or dissolved in a liquid or heated to create a stable, homogeneous ink with the desired and reproducible rheological (or flow) behavior. [1]

3D printing, direct ink-jet printing, and related approaches such as hot melt printing[2], involve patterning materials using a typical ink-jet print head, similar to one used in desktop printers. This approach requires wax-based inks that are heated during droplet formation and then solidify upon impact cooling. Cima[3] and Sachs[4] from Massachusetts Institute of Technology (MIT) pioneered the concept of using ink-jet printing to assemble materials.

Hot Melt (Phase-Change) Printing Technology

With thermal transfer printing and thermal wax transfer printing technology, phase-change inks (hot-melt inks or thermal waxes) are brought into contact with the substrate and a thermal head. The hot melt ink printer is a variant of DOD ink jet printers, where the liquid for the printing is obtained by melting the hot melt inks. Thermal transfer and hot melt printers utilize wax-like hot melt ink, rather than the liquid or dry ink used in other processes. The simplicity of thermal transfer printers leads to low equipment cost, cleanliness and high reliability. [5-11]

The thermal head is digitally addressed[12]. The process is generally binary, although some higher-end models are capable of producing multi-level dots on special thermal paper. This print image is stored as a pattern of dots and is reproduced by precisely timed and controlled exposure of the ink sheet to heating elements on a Thermal Print Head (TPH).

Phase-Change Inks

Inkjet printers use a few kinds of inks, either liquid inks with very low viscosity or solid inks with the phase-change ability occurring during the printing process. The hot melt inkjet inks have to stay solid at ambient temperatures, liquefy at the moment of printing and promptly solidify when reaching the substrate. When reaching a surface, the molten ink drop solidifies immediately, and prevents the ink from spreading or penetrating into the printed media. The quick solidification ensures that the image quality is good on a wide variety of recording media. [7,11]

Composition of Phase-Change Inks

Conventional hot-melt inks are composed from 4 main

components: an ink binder comprising a wax with a melting point in the range of 50°C to 90°C, which works as a ink vehicle, a resin, representative of tackifiers and adhesion promoters and different additives, such as antiscratch additives, adhesion and surface additives, antioxidants, biocides, plasticizers, and corrosion inhibitors designed to improve the ink's performance. Generally, hot melt ink contains a pigment or a dye functioning as a coloring component.[11]

Blowing Agents

The structure of cellular gas-filled polymers can be formed using two possible methods. Either by foaming a polymer system, by introducing gas-filled microspheres into a system, or by extracting material by a post-treatment, which results in the cell or pore formation. The most general classification scheme is based on the mechanism by which gas is liberated by blowing agents (BAs).

Chemical blowing agents (CBAs)

Chemical blowing agents are individual compounds or mixtures of compounds that liberate gas as a result of chemical reactions, including thermal decomposition, or as a result of chemical reactions of CBAs or interactions of CBAs with other components of the formulations. [13-15]

There are many options available when selecting a blowing agent. There are eight key materials used as blowing agents around the world. These include: azodicarbonamide (ADC); p, p'-Oxybis(benzenesulfonylhydrazide) (OBSH); p-toluene sulfonylhydrazide (TSH); 5-phenyltetrazole (5-PT); p-toluene sulfonylsemicarbazide (PTSS); dinitrosopentamethylene tetramine (DNPT); sodium bicarbonate (SBC); and zinc carbonate ($ZnCO_3$). [16]

Experimental

Materials

Various thermoplastic resins, waxes and alcohols, solid at ambient temperature, were used for formulation of inks for 3D structures.

Mixing

All of the inks were prepared the same way. The ingredients were mixed in a Lightnin® High Speed Mixer equipped with a mixing blade. The components were placed into a kettle, heated to about 85°C and the stirring was commenced. The kettle was heated to 120°C and stirring continued until a homogenized state of the mixture was achieved. The formulations were then cooled to ambient temperature at which they transitioned from the flowable to the non-flowable state.

Calorimetry

A Perkin Elmer Pyris 1 Differential Scanning Calorimeter (DSC) was employed for ink calorimetric analysis.

Viscometry

A Brookfield digital viscometer DVII with spindle #3 was used to measure hot melt inks flow viscosity. Ink temperatures were maintained at 130°C during the measurement.

Printability

The Fta32 Video 2.0 software from First Ten Ångstrom, Inc. was used to capture images of solid ink droplets and provided the printability analysis in terms of droplet height, contact angle, base area, etc.

Results and Discussion

Stage I – Thermal analysis of commercial hot melt inks

A very important property here is the sharp melting point of the phase change ink. The differential scanning calorimeter was used to obtain the range of melting temperatures for commercially produced hot melt inks used in thermal transfer desktop printers. The following figures represent melting characteristics of two different black hot melt inks, Black #1 (Xerox-set) and Black #2 (Media Science-set):

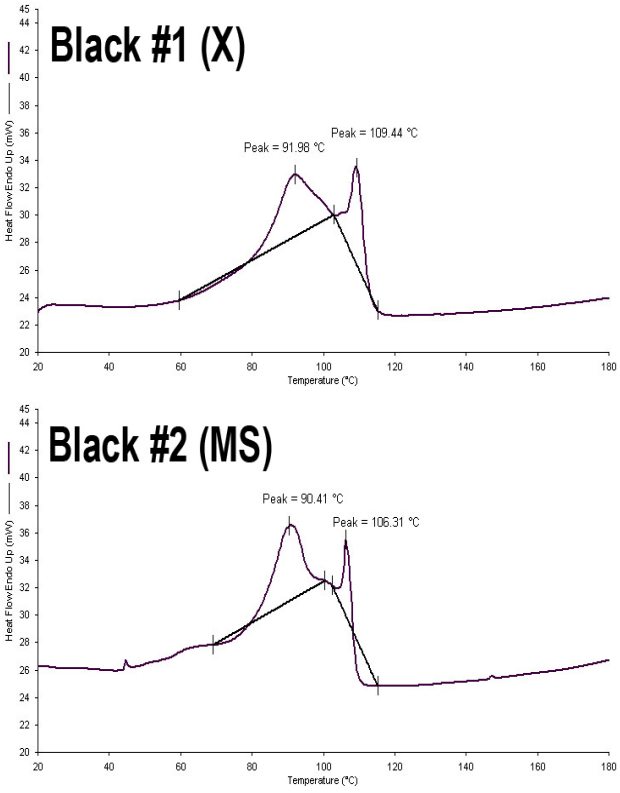

Figure 1: Thermal Analysis of Two Different Black Hot Melt Inks

The temperatures for all four process colors are shown in the Table 1. Both sets of inks show two melting peaks in the graphs. The melting points of these inks vary in the range of 90-110°C.

Table 1: Melting Temperatures of Different Ink Sets.

	Melting Temperature (°C)	
Set #1		
Cyan	87.32	105.90
Magenta	92.02	109.46
Yellow	91.48	109.19
Black	91.98	109.44
Set #2		
Cyan	90.73	105.39
Magenta	93.52	106.63
Yellow	95.39	104.76
Black	90.41	106.31

Stage II – Chemical blowing agents screening

The decomposition of the selected blowing agents must be higher than the ink melting temperature and also should not chemically react with other components. The blowing agent and thermoplastic polymers were selected according to the temperature in the print head (130-140°C), the viscosity requirements (~ 20 cPs @ 130°C) as well as the chemical compatibility of all ink components.

The selection of suitable bowing agents was carried out. Different blowing agents based on different chemistry were analyzed:

- azodicarbonamide (ADC);
- p,p'-Oxybis(benzenesulfonylhydrazide) (OSBH);
- Sodium bicarbonate (SBC).

Corresponding temperatures of decomposition are shown in the Table 2.

Table 2: Decomposition Temperatures of Different Blowing Agents

Name	Composition	Decomposition Temperature (°C)
Celogen® AZ 120	ADC	238
Ficel® HFVP 21	ADC/OBSH	183
Celogen® OT	OBSH	179

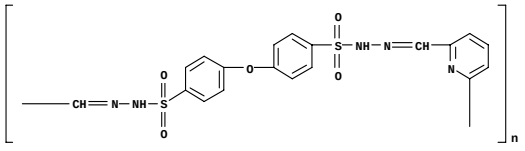

Figure 2: Chemical Structure of p,p'- oxybis (benzenesulfonylhydrazide)

The most fitting chemical blowing agent according to the thermal analysis has p,p'-oxybis (benzenesulfonylhydrazide) - OBSH. OBSH (Figure 2) is prepared by chlorosulfonation of diphenylether with chlorosulfonic acid and subsequent reaction with hydrazine in the presence of a base.

The blowing agent decomposition takes place at a temperature of approximately 179°C and the process is exothermic as shown in the graph below.

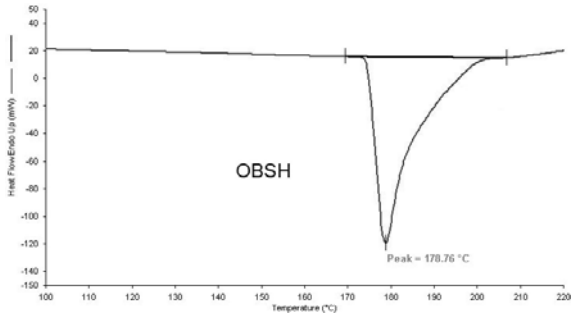

Figure 3: Thermal Analysis of p, p'-oxybis(benzenesulfonylhydrazide) Blowing Agent

Stage III – Novel hot melt inks composition

In this part of the work we formulated our own hot melt inks, which are combined with the selected blowing agents. The following components were used in the formulations of the hot melt ink (Table 3). (Pbw- parts by weight, (%)- weight percent of material in the formulation.)

Table 3: Composition of ink #5/101

No.	Component/Function	pbw	%
1	Paraffin wax/Ink vehicle	20.0	19
2	EVA/Imparts adhesion	10.0	10
3	Polyamide resin/Imparts adhesion	30.0	29
4	Low mol. alcohol I/Lower viscosity	40.0	39
5	Blowing Agent/Gas release	2.8	3
	Total	**102.8**	**100.0**

When a small volume of the molten ink was dropped onto a paper substrate, the resulting solidified ink drops were too brittle and did not have sufficient adhesion to the substrate. Alternations in the formula were then made (Table 4). To improve adhesion, we increased the amount of polyamide resin and discarded the EVA component from the formula.

Table 4: Composition of ink #6/101

No.	Component/Function	pbw	%
1	Low molecular PE wax/Ink vehicle	3.5	3.1
2	Polyamide resin/Imparts adhesion	68.0	59.4
3	Low mol. alcohol I/Lower viscosity	40.0	34.9
4	Blowing Agent/Gas release	3.0	2.6
	Total	**114.5**	**100.0**

The ink possessed improved hardness and better adhesion after deposition. Unfortunately, there was loss of adhesion observed over time.

Another modification was made to the formula (Table 5). The use of hydrogenated rosin resin as a tackifier was considered. In order to reach low viscosity target we increased the low molecular alcohol ingredient parts.

Table 5: Composition of ink #22/104

No.	Component/Function	pbw	%
1	Carnauba wax/Ink vehicle	4.0	3.9
2	Polyamide resin/Imparts adhesion	20.0	19.6
3	Low mol. alcohol I/Lower viscosity	25.0	24.5
4	Low mol. alcohol II/Lower viscosity	25.0	24.5
5	Hydrogenated rosin ester/Tackifier	25.0	24.5
6	Blowing agent/Gas release	3.0	2.9
	Total	**102.0**	**100.0**

The resultant ink showed satisfactory adhesion and hardness. The viscosity of the ink at 130°C was in the acceptable range as well (15-20 cPs). Figure 4 shows the thermal trace of the ink composition. The melting temperatures of all the ink components are listed in Table 6.

Table 6: Melting Temperatures of Ink Ingredients

Component	Melting Temperature (°C)
Carnauba wax	**85**
Polyamide resin	**127**
Low molecular alcohol I	**63**
Low molecular alcohol II	**56**
Hydrogenated rosin ester	**77**
Blowing agent	**179**

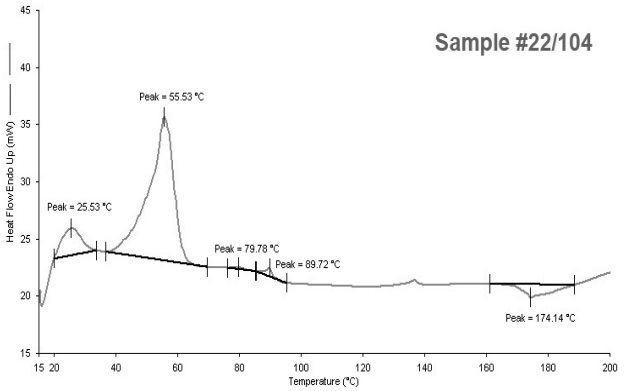

Figure 4: Thermal Analysis of Ink Sample #22/104

From the DSC analysis, the melting points of the ink components and the decomposition point of the blowing agent can be seen. The hot melt ink formula has a melting temperature well segregated from the decomposition point of the blowing agent. Also, it was found that the peak for the polyamide resin, which should decompose at 127°C, was not present in the graph. We presume that polyamide resin might react with one of the ink components, most likely with low molecular alcohol II, and form some other substances. Apparently, there is a peak showing a melting point at 25°C. This peak doesn't correspond to any of the chemicals used in the formula. From additional experiments that were carried out, we realized that the presence of the low molecular weight alcohol II is responsible for presence of the unusual peak and most likely it is causing fuming at low temperatures.

Although the final ink performed better than the previous one, the final properties were still not as good in quality as expected, e.g. , flake appearance, fuming, viscosity of 24 cPs at 130°C. The additional modifications were made to reach the desired properties of the ink. The final formulation does not include the alcohol and accordingly exhibits enhanced overall performance (Table 7).

Table 7: Composition of ink #23/101

No.	Component	pbw	%
1	Carnauba wax/Ink vehicle	5.0	5.0
2	Polyamide resin/Imparts adhesion	17.0	17.0
3	Low mol. alcohol I/Lower viscosity	50.0	50.0
4	Hydrogenated rosin ester/Tackifier	25.0	25.0
5	Blowing agent/Gas release	3.0	3.0
	Total	**100.0**	**100.0**

Figure 5 illustrates a differential scanning calorimeter trace of the ink. All the corresponding melting temperatures of the ink components are listed in the Table 6.

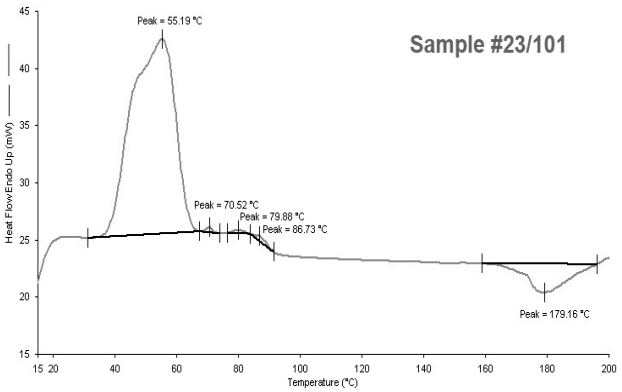

Figure 5: Thermal Analysis of Ink Sample #23/101

As seen, the resulting hot melt ink formula has a melting temperature and the decomposition of the blowing agent separated with temperature gap of 90°C. Note that the blowing agent decomposition is exothermic at temperature of approximately 179°C. The gap seems to be too big for the research purpose. The components of the ink show sharp peak when melting (~ 55°C) followed by additional peaks in the temperature range from 70–87°C. From our composition, we can say that the melting temperature of the

ink is little bit lower than the commercial ones (Figure 1). The viscosity of the final hot melt ink was found to be 19 cPs at 130°C and ink had good adhesion to the substrates.

Fta32 Video 2.0 software was used to capture images of two final inks (Figure 6). The simulated droplets were created by deposition of molten inks on the regular paper substrates using the micropipettes. Fta32 Video 2.0 also provided the printability analysis in terms of height, contact angle, base area, etc (Table 8).

Figure 6: Sample #2/2104 (left) and Sample #23/101(right)

Table 8: Printability Results

Component	Sample #22/104	Sample #23/101
Contact Angle (deg)	67.97	60.16
Base (mm)	3.21	3.54
Base Area (mm^2)	8.11	9.84
Height (mm)	0.553	0.477

Conclusions

The formulation of hot melt inks with addition of blowing agent was carried out. It was found that the linear alcohols reduce the melt viscosity of inks. In addition, the melting temperature is shifted towards lower values by incorporation of these alcohols into the formulation. They probably react with other ink components and cause fuming of the inks. Therefore, in further work, inks with altered low molecular linear alcohols were formulated. These inks showed better heat stability and sufficiently low viscosity (19cPs at 130°C). In further work, different blowing agents will be evaluated. In addition, the surface tension of the ink needs to be modified in order to achieve proper ink/substrate interaction. Differential scanning calorimetry was found useful in evaluation of thermal behavior of novel phase change inks.

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