Laser Printing of Polymeric Materials

Mr Soumya Banerjee & Prof. David IanWimpenny
Rapid Prototyping & Manufacturing Group
Faculty of Computing Sciences & Engineering,
DeMontfort University, Leicester,UK
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Electrophotography, the basis of photocopying and laser printing, is a reliable and well developed method of precisely depositing fine powders to form text or images. The process is highly adaptable to different types of materials; commercial toners are based on particular polymers but researchers have already shown the potential to deposit other materials including metals and ceramics. Once the powder layer has been deposited it can be heated to form a fused layer.

This paper describes research conducted at DeMontfort University to develop a range of toners based on conventional engineering polymers and concludes by outlinning the challenges which will be tackled in the next phase of research.

1. Introduction

Standard laser printers work on the principle of electrophotography, where fine polymeric toner powder is picked up and precisely deposited on a substrate, usually paper, using electrostatic forces. Normally four basic colour toners (black, yellow, cyan and magenta) are used in standard colour laser printer. To generate a colour picture these 4 toner materials are applied in a precise pattern to form a layer of toner on the page, typically 8-12 microns thick, depending on the configuration and age of the printer.

For layer manufacuting applications laser printing may offer some important advantages, particularly for the generation of functionally graded structures. Laser printing is a dry process and has a very high deposition efficiency compared to ink jet printing of powders in a liquid carrier, for example. Moreover, laser printing is, in principle, highly adaptable to other forms of toner materials including thermoplastics, cermics and metallic powders.

The speed of the desktop laser printer can range from 8 to 24 ppm (pages per minute) with resolution from 300 to 600 dpi. However, industrial laser printers can print up to 1000 ppm, with a resolution of 1200 dpi. Crucially, for layer manufacturing applications, laser printing techniques can be used to deposit relatively thick (20 microns or more) layers of toner. Once the toner has been deposited it is fused to form a solid layer, typically by contact with heated rollers or via infrared radiant heating.

The potential application of laser printing in layer manufacturing has been recognized by several other researchers (Bynum[1], Grenada [2], Cormier[3] and Kumar[4]). Earlier research by Kumar [5,6] explored the feasibility of generating objects by depositing multiple layers of standard toner materials by laser printing. This research has focused on the problem of static charge depletion, which limits the Z height of any object produced using conventional laser printing (based on charging of the substrate) to just 1-2mm.

Work by other researchers has focused on using standard commercially available toners to generate objects by laser printing. Cormier [3], however, found that it is possible to successfully deposit High Density Polyethylene (HDPE) powders using a HP LaserJet 4 printer. The research conducted at DeMonfort University, described in this paper, aims to investigate the observations made by Cormier and moreover to extend the range of polymers to include both Polypropylene (PP) and Low Density Polyethylene (LDPE). In addition to conducting trials using the HP LaserJet 4 printer the technical viability of manufacturing suitable thermoplastic toners via conventional toner manufacturing methods and the development of new toner production methods using off-the-shelf polymeric powders has been undertaken and is presented.

2. Electrophotography Process

Electrophotography is a powder printing technology where powder is picked up and deposited using electrostatic forces. The core component of the laser/LED based electrophotography is **photoreceptor,** typically a revolving drum or belt. This is made out of a **photoconductive** material which can be charged by exposure to an electrical field and then parts of the surface selectively discharged by exposure light (laser beam or LED array). In the laser printing process, an electrostatic image is produced on the photoreceptor by charging and selective discharging. The surface of the drum is then coated with a fine layer of powdered toner material, depending on the charged area, and then this latent image is transferred to the paper and fused to form the printed text/image.

The laser based electrophotography process requires five stages to complete one printing cycle:

1. **Charging the photoconductor**: Photoreceptor surface is charged with corona discharge device, for example.
2. **Exposure to light**: The charged surface is exposed to a light source of a suitable wavelength (laser/arrays of LED) selectively discharging areas of the photoreceptor.
3. **Development**: Charged powder (toner) is brought close to the photoconductor and it adheres selectively on the discharged areas of the surface.
4. **Image transfer**: Toner is transferred from the photoconductor drum onto paper by application of an electrostatic field or hot/cold pressing.
5. **Fusing of Toner**: The toner is subsequently fused thermally to fix it on the paper.

2.1 Printer Cartridge :

The design of the print cartridge is critical for successful printing and the configuration (electrical arrangement, voltage levels, roller mechanism) of each cartridge is different for each particular print engine. In the case of the HP LaserJet 4 the print cartridge contains all of the major components of the electrophotography process (except high voltage supply, laser and fusing roller), the printer its self is largely concerned with paper handling.

Toner is generally brought forward from the hopper towards developer roller by agitating the toner particles inside the cartridge by rotating rollers inside the cartridge (see Figure 1). The surface of the 'developer roller' is coated with the toner before it is being "pulled-off" from the developer roller onto the organic photoconductor drum (OPC) via electrostatic force .The toner is finally deposited from the drum on to the substrate (paper) via electrostatic force. A doctor blade meters the amount of toner particles transferred to the developer roller and also plays an important role in charging the toner particles. .

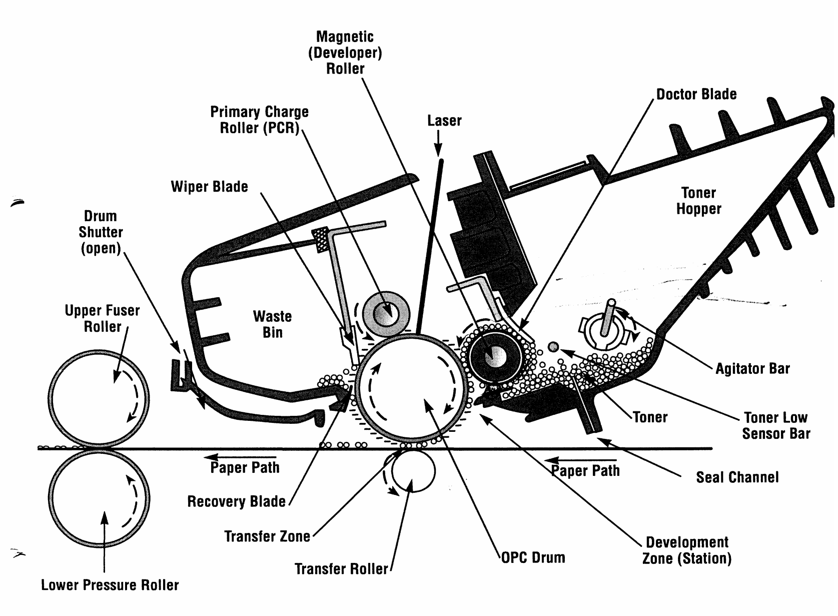


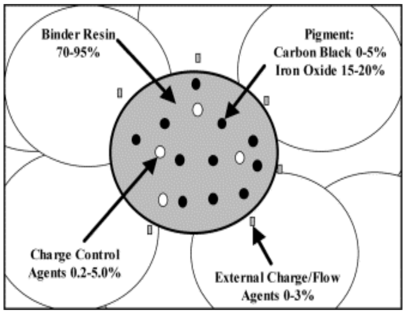
Figure 1: HP LaserJet 4 toner cartridge in section

3. Standard Toner Materials

Toner is a dry pigmented complex powder with particles size of 8-12 micrometer and is composed of the following basic components (see Figures 2 and 3);

- Polymer - generally brittle to enable efficient particle manufacture and low melting point to enable rapid thermal fusing.
- Colorant (pigments e.g carbon black) - to provide the desired toner colour.
- Charge control agent – to enable the charge characteristics of the toner to be fine tuned.
- Flow control additives (for example fumed silica) – to prevent the toner from caking.
- Wax – to prevent toner from sticking to the heated fuser rollers.

Each toner is formulated to match the characteristics of a particular print engine, including the toner cartridge configuration, image development, transfer mechanism and fusing technique. Tribo-electric charging of the toner is an important factor for printing [7][8]and is influenced by the type of polymer, the toner particle size and shape, polarity, pigment and surface additives (typically silica, titanium oxides, organo-metallic salts) see Figure 2. The purpose of using surface additives is to maintain the tribo-charging characteristics, transparency and flow characteristics of each toner particle.



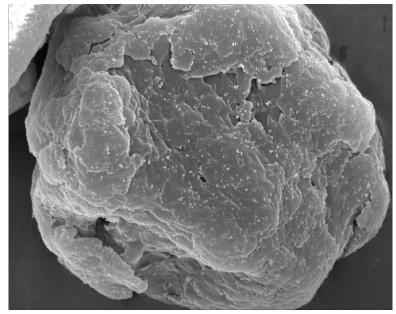


Figure 2: Composition of laser printer toner   Figure 3: SEM image of a standard toner particle

Standard toners are mostly made from styrene acrylic co-polymer/polyester resin having very low melting temp and are very brittle. Toners can be of two type; either mono component or dual component. Commercial desktop printers generally employ mono component toners. Mono component toners can be further classified as resistive magnetic (e.g HP/Canon) and resistive non-magnetic (e.g Lexmark). Magnetic toners have a significant proportion of iron-oxide additive (30-60%), which tends to make them relatively brittle and dark in colour thus limiting their use to black toner. The research presented here is limited to mono component toner formulations and associated hardware.

4. Toner Manufacturing Processes

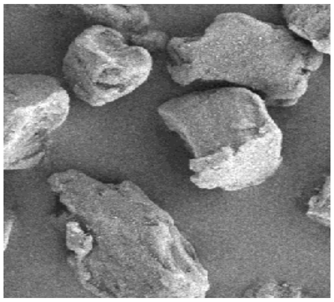
Toners can be produced either by conventional mechanical milling (pulverization) process or via the recently developed chemical polymerization process.

4.1 Pulverizing Process

The traditional mechanical milling (pulverizing) process involves blending of resin, charge control agent, wax, pigment and iron oxide. This blended material is then heated until the polymer is fully melted and extruded. After sufficient cooling, it is crushed and granulated into smaller particles. The granulated material (3-5mm diameter) is further ground by air jet milling to produce fine particles which are passed through a classifier unit to ensure a relatively tight control of the size of the toner particles (8-10 microns). Finally, the particles are coated with surface additives, such as fumed silica, using a specialised mixing process.

4.2 Chemical Process

Wet chemical toner processes, such as suspension polymerization and emulsion polymerization, are used to produce toners particles directly without any milling process. This process provides much better control of the size and shape of the toner particles. The smaller, regular, spherical particles of polymerized toners have improved flow characteristics and higher toner transfer efficiency from drum to the paper, thus giving improved image quality (See Figure 4 and 5 below). Canon uses suspension polymerization where as Xerox/Konica uses emulsion polymerization techniques. Unfortunately, to develop a polymerized toner requires significantly more investment than for a pulverized toner and at present the process is limited to only a few polymer types (styrene acrylic, polystyrene, polymethylmethacrylate).



10 microns

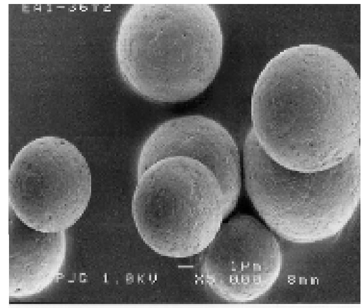


Figure 4: Conventional Toner (Lexmark C510)   Figure 5: Chemical Toner

5. Thermoplastic Toner Development

To establish a benchmark, against which future results can be compared, trials were undertaken to deposit multiple layers of standard magnetic toner using a HP LaserJet 4. As predicted these samples were extremely fragile and surface cracking was observed after just 10 layers (see Figure 6).

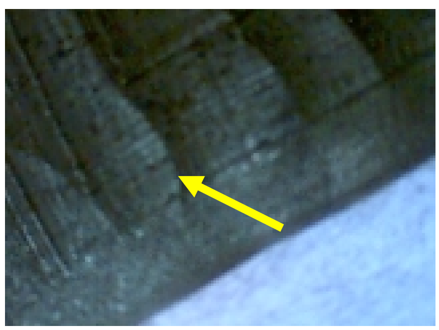


Figure 6: Surface cracks after 10 prints with standard magnetic toner using a HP LaserJet 4 printer.

To produce toners using standard engineering thermoplastic materials a suitable manufacturing route was investigated.

5.1 Polymer Grinding Trial

Initial trials were conducted to assess the potential to produce toners by conventional mechanical pulverization.

The air-jet milling process was used to reduce the starting feed-stock (2-3mm diameter granules) for each material to give 10 micron particles. During the air milling test, the air flow was maintained at 135 m^3 per hour at 6 bar pressure with a rotor speed of 11,500 rpm. Each sample was subjected to the grinding environment for approximately 30 minutes. It was found that for all the engineering polymers only 20 to 45 percent of the sample had been reduced to below 10 micron in diameter, compared to more than 80% efficiency for a conventional brittle toner material (see Figure 7).

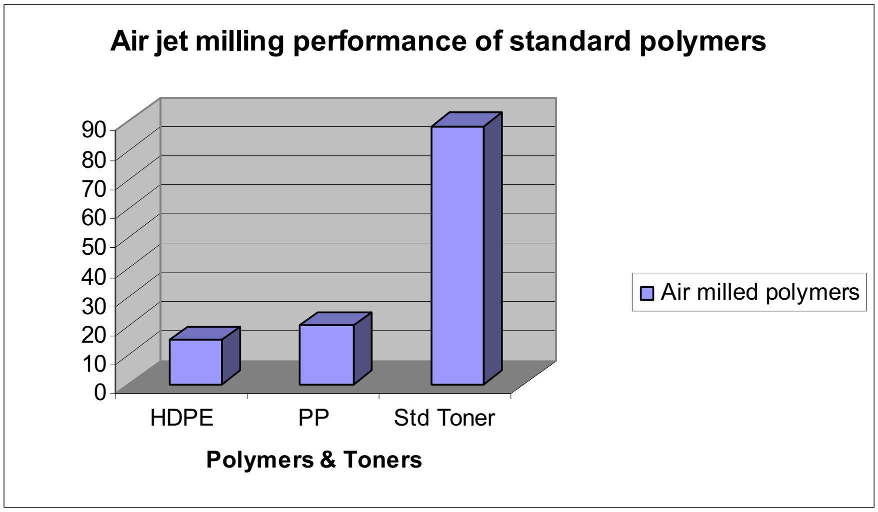


Figure 7: Air milling performance (% efficiency) of different polymers

Grinding trials were also performed using ball milling, centrifugal milling and cryogenic grinding Unfortunately, none of the methods used were able to efficiently produce fine powder (10 micron or below) from the engineering polymer granules.

5.2 Surface Treatment of Polymer Particles

Given that grinding of tough polymers has been shown to be extremely difficult an alternative route for generating tough thermoplastic toners is required. One alternative is to use off-the-shelf thermoplastic powders (10 micron particles produced by a chemical route) and then to apply the additives required for laser printing through a surface coating technique.

In this experiment several standard surface additives were investigated (charge control and flow control agents) but the primary trials were conducted using fumed silica (170 to 250 nanometers) as a flow control agent. Samples of LDPE, HDPE and PP powder were sourced for the trial (see Table 1).

Polymer	Melt - index	density
HDPE	10	0.952
LDPE	4.7	0.923
PP	35	0.909

Table 1 : Melt index and density of polymers used for the trials

No colour pigments and wax were added to the core polymer particles for these trials. The speed of rotation and geometry of mixing blades were carefully selected to encourage even coating of the entire sample. A critical factor was to check whether any coagulation takes place of polymer particles due to the heat generated during mixing, particularly at the higher mixing speeds.

Initial trials were conducted with 1- 2% fumed silica (by weight) to determine the mixing parameters to give the best coating efficiency. Different mixing blades assessed (see Figures 8 and 9) and it was found that the "paddle type" blades gave better mixing efficiency than "shear type" mixing blades. This is due to resultant vector of three velocity components in the horizontal and vertical plane during rotation which encourages circulation of the entire powder samples through the mixing area. The rotational speed of the mixer was controlled between 1200-2000 rpm and mixing process was closely monitored to ensure that no coagulation took place due to overheating.

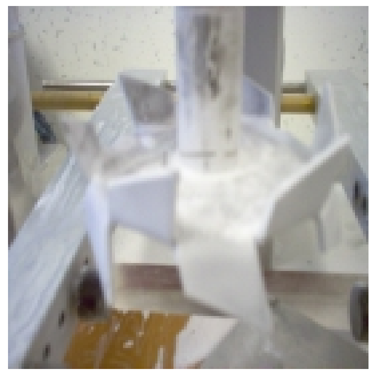
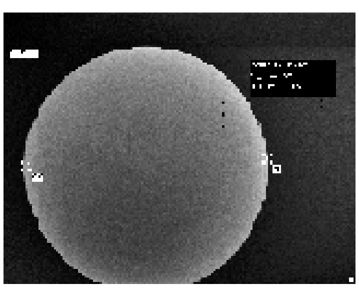


Figure 8: Toner mixer

Figure 9: Paddle type mixing blade

Samples were then inspected using a scanning electron microscope (SEM) to assess if the polymer particles were adequately coated with surface coating agents. It was found that using this approach the surface of polymer particles could be evenly coated with the required additives to enable effective laser printing (see Figures 10 and 11).



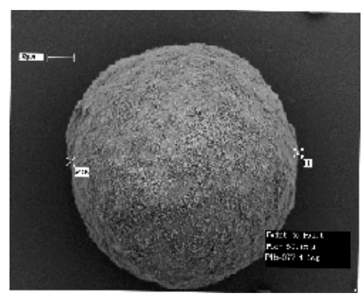


Figure 10: Uncoated LDPE particle

Figure 11: Surface coated LDPE particle

5.3 Printing Trials

These trials were performed to investigate the observation made by Cormier [3] that HDPE can be printed using a HP LaserJet 4 printer and to assess the ability to print other polymers, including LDPE and PP.

Samples were prepared with particle sizes and charge distribution ranging from 8 to 25 micron and 0 to 20 micro-columb/gm respectively.

A standard print cartridge (HP 92298X), suitable for a HP LaserJet4, was modified to enable it to be easily refilled with alternative toner materials. It was found that it was possible to print HDPE, LDPE and PP based toners using the HP LaserJet 4 provided that particles were treated with 1-2% flow control agent (see Figures 12,13,14)..

Although these results were very promising it was also observed that there was significant "leakage" of toner from the cartridge, contaminating both the printer and the substrate (paper). Also the efficiency of deposition was lower than the standard magnetic toner supplied for this print engine.

Indeed the source of the problem was traced to poor initial coating of the developer roller. It was also observed that print efficiency varied significantly between the different polymer samples tested.

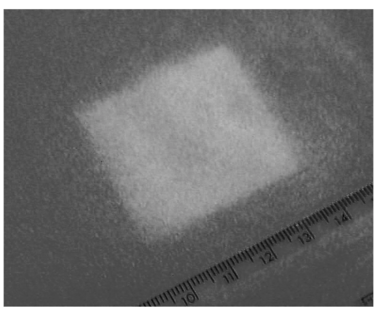


Figure 12: Laser printed HDPE

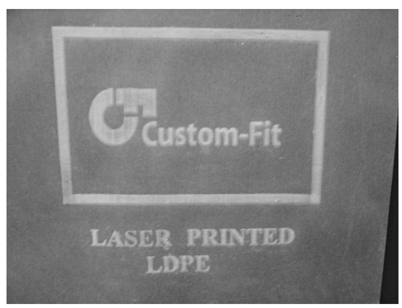


Figure 13: Laser printed LDPE

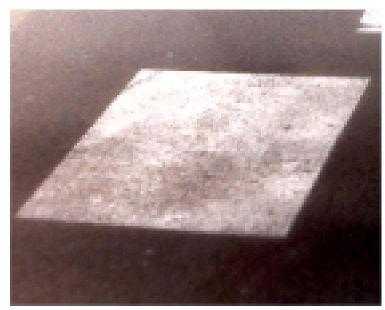


Figure 14: Laser printed PP

6. Discussion

Toner development is generally a very complex procedure, based largely on an empirical "feel" for the correct formulation, acquired after many years experience in the field. The demands presented by different aspects of the process are often in direct conflict with each other. Moreover, the slightest deviation from the standard operating characteristics of the toner formulation can lead to a complete halt to printing and may even result in damage to the print engine. The range of standard toner polymers is very limited and so the introduction of a completely new host of thermoplastic materials, represents a significant challenge, even for experienced toner developers. HDPE, LDPE and PP based negatively charged non-magnetic toners were successfully printed using a magnetic laser print engine. This is completely contrary to accepted logic. Given that the normal magnetic attraction of the toner to the developer roller can not come into play, as the toner has no magnetic component, the deposition of the new toner is completely unexpected. One possible explanation is that the image development is occurring in a non magnetic mode, through friction (rubbing) induced tribocharging between the toner and the doctor blade. Further tests are required to confirm this.

This work has confirmed the observation made by Denis Cormier (2002) that HDPE can be successfully printed using the HP LaserJet 4 printer. Moreover, two completely new thermoplastic materials LDPE and PP have also been tested and proven to print in a similar manner. Interestingly Cormier observed printing of standard HDPE polymer which was not coated, however, trials indicate that pure HDPE can not be successfully printed and surface coating by fused silica is required. It is very likely that the HDPE material used by Cormier had already been treated with flow control agents to enable it to flow during processing (rotational moulding).

One of the most important factor for printing a toner is its particle size and shape (this influences the charge-to-mass ratio and the flow/adhesion characteristics of the toner). The standard size of conventional toner particles it 8 to 10 micron in diameter but this is very difficult to achieve for tough thermoplastic polymers (such as HDPE, LDPE and PP) using conventional milling techniques due to the extremely poor milling efficiency. The potential to combine the necessary additives by surface coating, through carefully controlled mixing, has been demonstrated in these trials. In the long-term, however, it may be more effective to develop new polymerised toners which incorporate some of the required additives during original manufacture of the particles. This is, however, primarily a commercial rather than technical challenge due to the attendant development costs. In the meantime surface coating provides an effective method of new materials development.

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